UTAH DEPARTMENT OF ENVIRONMENTAL QUALITY

MERCURY SOURCE PROTOCOL

April 2008

PREFACE

This protocol has been prepared by the Utah Department of Environmental Quality. This protocol supports a Department-wide effort to address several questions concerning mercury contamination in the State of Utah and to provide methodologies that may be used to help identify sources of mercury to lakes and rivers throughout the State. Sections 1 through 3 give an introduction to the mercury problem in the environment and Utah, discuss sources of mercury, and familiarize the reader with interactions of mercury in the environment. Section 4 describes how to use this protocol to determine the source of a mercury problem. The section is based on the phased approach called for in the Utah Department of Environmental Quality Mercury Source Assessment Protocol Concept. Section 5 follows with the methodologies for sampling and characterizing mercury in the various media of concern. These sampling and analytical methodologies are backed-up by a Quality Assurance Project Plan with referenced SOPs in the Appendix. The protocol concludes with Section 6 that discusses preventive measures, and Section 7 that provides a reference list.

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LIST OF ACRONYMS

BrCl   Bromine monochloride
CAIR   Clean Air Interstate Rule
CVAFS   Cold-Vapor Atomic Fluorescence Spectrometry
DQO   Data Quality Objectives
DEQ   Department of Environmental Quality
DSHW   Division of Solid and Hazardous Waste
GPS   Global Positioning System
HCl   Hydrochloric Acid
Hg^0 Elemental Mercury
HgII   Divalent Mercury
$HgII_{aq}$ Divalent Mercury – Aqueous
$HgII_g$ Divalent Mercury – Gaseous
Hg_p Mercury – Particulate
HgS   Mercury Sulfide
LC_{50} Lethal Concentration 50
MDL   Minimum Detection Level
MDN   Mercury Deposition Network
MeHg   Methylated Mercury
ML   Minimum Level
MS/MSD   Matrix Spike/Matrix Spike Duplicate
MSW   Municipal Solid Waste
NADP   National Atmospheric Deposition Program
NDEP   Nevada Department of Environmental Protection

PARCC	Precision, Accuracy, Representativeness, Completeness, and Comparability
PPM	Parts Per Million
QA/QC	Quality Assurance/Quality Control
QAPP	Quality Assurance Project Plan
RBP	Rapid Bioassay Protocol
RfD	Reference Dose
RGM	ReactiveGaseous Mercury
SAP	Sampling and Analysis Plan
SOP	Standard Operating Procedure
SPLP	Synthetic Precipitation Leachate Procedure
T&E	Threatened and Endangered
UNR	University of Nevada Reno
USEPA	United States Environmental Protection Agency
USFWS	United States Fish and Wildlife Service
USGS	United States Geological Survey
YOY	Young of the Year

MERCURY SOURCE PROTOCOL

1.0   INTRODUCTION

Mercury contamination in the State of Utah has prompted the Utah Department of Environmental Quality (UDEQ) to address this issue and develop a protocol and methodologies to help identify sources of mercury contamination in the State. This effort is in part being conducted as a result of fish consumption advisories issued for mercury beginning in August 2005 These advisories indicate that mercury is present in surface water bodies in Utah and is being ingested by organisms and bioaccumulating up the food chain. This protocol and subsequent implementation of the protocol may be used to answer key issues developed in the "Utah Department of Environmental Quality Mercury Source Assessment Protocol Concept" (UDEQ, 2006):

- Where is the mercury coming from;
- What is the ultimate source of the mercury that is showing up in Utah's fish population and presenting a human health concern;
- Can the sources be identified; and
- If the sources can be identified, what can be done to reduce or eliminate these sources of mercury?

The discussions in this protocol describe the methodology(s) to efficiently characterize mercury contamination, to determine the likely source(s) of mercury to a water body, discuss potential sources for mercury, including natural and anthropogenic sources, and identify the pathways of mercury contamination in the environment. Using data on how mercury behaves in the environment and where and in what form/speciation mercury is present in various media, potential sources for the identified mercury contamination may be identified.

The protocol is designed to be implemented in phases, following the tiered approach outlined in the "Utah Department of Environmental Quality Mercury Source Assessment Protocol Concept." The phased approach is deemed necessary, as some decision points will require data from previous steps. This phased approach will also be designed to maximize resource utilization and minimize costs. Details are provided in Section 4.

1.1   What Is Mercury

Mercury is a naturally occurring metallic element that is found in soil, air, and water. Mercury is present in many forms such as elemental or metallic mercury, inorganic mercury compounds, and organic mercury compounds. Mercury combines with elements, such as chlorine, sulfur, or oxygen to form inorganic mercury compounds or may combine with alkyl and aryl organic groups to form organic mercury compounds. The most common and prevalent form of organic mercury in the environment is methylmercury. Methylmercury is produced by microscopic organisms that convert

inorganic mercury in the soil and water into methylmercury. Thus, the more mercury that is present or released into the environment, the more chance that methylmercury is produced by these organisms. When assessing how mercury behaves in the environment, methylmercury is important as it bioaccumulates in the food chain.

1.2   Mercury Health Issues and Toxicity

Mercury is a highly toxic heavy metal. Even at low levels, mercury can affect the central nervous system and in particular, the brain. At higher levels of mercury, other organs, such as the kidneys, are susceptible to damage. Studies have shown that children and developing fetuses are at a higher risk for developing problems when exposed to mercury. Methylmercury and metallic vapors are the most harmful forms of mercury in that these forms easily reach the brain (ATSDR, 1999).

As outlined in USEPA 2005a, the USEPA has set a health-based ingestion rate for chronic oral exposure to methylmercury (1.0E-04 mg/kg-day (USEPA, 2006b)), termed an oral Reference Dose (RfD). The RfD is an estimate (with uncertainty spanning perhaps an order of magnitude) of a daily exposure to the human population (including sensitive subgroups) that is likely to be without an appreciable risk of deleterious effects during a lifetime (USEPA, 2002). It is the belief of the USEPA that exposures near or below the RfD are very unlikely to be associated with appreciable risk of deleterious effects. However, it is important to note, however, that the RfD does not define an exposure level corresponding to zero risk; mercury exposure at or below the RfD could pose a very low level of risk which USEPA deems to be non-appreciable. It is also important to note that the RfD does not define a bright line above which individuals are at risk of adverse effect.

1.3   Ecotoxicology of Mercury in Freshwater Aquatic Systems

Mercury has varying ecotoxicological effects on freshwater aquatic organisms, being a mutagen, teratogen, and carcinogen to ecological species. The toxicity of mercury varies for different organisms based on the form of mercury in the aquatic environment, the dose to the organism, and the route of mercury exposure, as well as the sex, life stage, and general condition of an organism. There are numerous abiotic and biotic processes that can affect mercury toxicity, but the mechanisms of action for these factors are not all well understood (Eisler, 1987).

Organic mercury, specifically methylmercury, is generally the form most toxic to aquatic organisms, as uptake of organic mercury by aquatic species is generally greater than for inorganic compounds, and organic mercury is less readily excreted. Methylmercury is produced through bacterial methylation, a process where relatively less toxic forms of mercury are transformed in both aerobic and anaerobic environments (http://www.epa.gov/region5superfund/ecology/html/toxprofiles.htm#hg).

Methylmercury can be highly toxic to aquatic organisms, and can biomagnify. For example, fish can contain concentrations of methylmercury in tissues up to 100,000 times ambient water concentrations (Eisler, 1987). Methylmercury can also bioaccumulate, and can be retained for long periods of time in tissues. Birds and mammals that eat contaminated fish are at risk of accumulating and retaining concentrations of methylmercury, and can, as a result, represent an exposure to upper-level ecological predators.

Mercury exhibits varied toxicological effects on bird species, including effects on reproduction, growth, and survival, with organomercury compounds exhibiting greater toxicological responses and longer biological half-lives. Mercury appears to concentrate in the liver and kidneys of birds. Piscivorous birds tend to have higher concentrations than non fish-eating birds. Impacts to mammals exposed to mercury can include changes in behavior, neurological activity, and reproduction difficulty (http://www.inchem.org/documents/ehc/ehc/ehc086.htm).

As previously stated, mercury can impact aquatic organisms in various ways, based on the form of mercury, and the organism. The following is a brief synopsis of mercury toxicity to different aquatic receptor groups.

1.3.1   Microorganisms

Mercury represents a major hazard to microorganism at low concentrations. Inorganic mercury show effects to microorganisms at levels of 5µg/L in culture media, with organomercury compounds exhibiting effects at concentrations 10 times below this level. Mercury is bound to cell walls or membranes of microorganisms and toxicity of mercury is related to both cell density and the concentration of mercury in surrounding substrates. The effects of mercury on microorganisms are often irreversible. (http://www.inchem.org/documents/ehc/ehc/ehc086.htm).

1.3.2   Aquatic Plants

Mercury can impact aquatic plants in a variety of ways across a wide range of concentrations, including survival and growth. These impacts are partially related to disruption of the photosynthesis process. Organic forms of mercury are more toxic to aquatic plants than inorganic forms. Sediment and humic materials can reduce the availability of mercury to aquatic plants due to adsorption. Aquatic plants have been shown to sustain damage from exposure to inorganic mercury at concentrations of 800 to 1200 µg/L, with toxic effects observed from organomercury at concentrations 10 to 100 times lower (http://www.inchem.org/documents/ehc/ehc/ehc086.htm).

1.3.3 <u>Aquatic Invertebrates</u>

Toxicity of mercury to aquatic invertebrates is controlled by various factors, including the concentration and species of mercury, the developmental stage of the invertebrate, temperature, salinity, water hardness, and water flow rates. Methylmercury is the most toxic form to aquatic invertebrates, with the larval life stage representing the most sensitive portion of the life cycle. Organic compounds are toxic to these organisms at concentrations ranging from 10 to 100 times below levels of inorganic mercury. Increases in water temperature and decreases in hardness increases mercury toxicity to these organisms, and toxicity appears to increase in flowing systems versus static systems. Decreases in salinity also appear to increase toxicity. Mercury levels of 1 to 10 µg/L have been noted to result in acute toxicity to aquatic invertebrates (http://www.inchem.org/documents/ehc/ehc/ehc086.htm).

1.3.4 <u>Fish</u>

Inorganic mercury is toxic to fish at low concentrations, with 96-h LC_{50} (lethal concentration 50%) values ranging between 33 and 400 µg/L. Organic mercury is approximately 10 times more toxic to fish than inorganic mercury. Mercury toxicity to fish is controlled in part by water temperature, salinity, dissolved oxygen, and water hardness, and life stage, with larval fish appearing more sensitive than other periods in the life cycle. Fish are up to 100 times more sensitive to mercury in flow-through toxicity tests than in static testing conditions.

Sublethal concentrations of mercury have been shown to cause physiological and biochemical abnormalities. Mercury toxicity also impacts reproduction in fish species. Mercury tissue concentrations in fish appear to be related to the age of the organism, and in some cases, depending on the sex, with males maintaining higher mercury levels than females. See (http://www.inchem.org/documents/ehc/ehc/ehc086.htm).

Some researchers have developed a statistical model for predicting mercury concentrations in fish tissue (Qian., S. et.al., 2001). They found the important factors for predicting mercury fish tissue concentrations are location, species, water body pH, and fish weight. Other predictor variables include proximity to sources of mercury, and environmental factors affecting mercury movement and transformation.

Some additional articles on mercury in fish should be consulted by the interested reader (Stafford C., et al, 2004), (Sveinsdottir, A., et al., 2005).

1.4   Consumption Advisories

USEPA indicated in the *Mercury Study Report to Congress* (USEPA, 1997a) that the typical consumer was not in danger of consuming harmful levels of methylmercury from fish and was not advised to limit fish consumption on the basis of mercury content. This

advice is appropriate for typical consumers who eat less than 10 grams of fish and shellfish per day with mercury concentrations averaging between 0.1 and 0.15 ppm. At these rates of fish intake, methylmercury exposures are considerably less than the RfD of 1E-04 mg/kg-d. However, eating more fish than is typical or eating fish that are more contaminated can increase the risk to a developing fetus (USEPA, 2001). A fish consumption advisory is issued when levels of mercury in fish are above a concentration of 0.3 ppm. In the State of Utah fish consumption advisories for mercury have been issued for the following water bodies:

Utah Mercury Fish Advisories (as of April 2007)		
County	**Site**	**Fish Species**
Emery	Joes Valley Reservoir	Splake Trout
Garfield	Calf CK above Campground	Brown Trout
Grand	Grand County	Brown Trout
Iron	Newcastle Reservoir	Rainbow Trout
Morgan	Weber R below Morgan Lagoons	Brown Trout
Uintah / Carbon	Green River in Desolation Canyon	Channel Catfish
Wasatch	Jordanelle Reservoir	Brown Trout
Washington	Upper Enterprise Reservoir	Rainbow Trout
Washington	Gunlock Reservoir	Large Mouth Bass

Complete information with specific advisory detail and maps of the affected areas can be found at the following URL: http://www.fishadvisories.utah.gov/(UDEQ, 2007)

Similar advisories in 2005 and 2006 have been issued for waterfowl in the vicinity of the Great Salt Lake due to high concentrations of methyl mercury in Northern Shoveler, Common Goldeneye, and Cinammon Teal. For more information, see http://www.deq.utah.gov/Issues/Mercury/duck_advisory.htm

Table 1-1 summarizes USEPA regulations and advisories related to Hg in various media.

Table 1-1. USEPA Regulations and Advisories. (USEPA 2003)

- Maximum Contaminant Level inorganic mercury in drinking water = 0.002 mg/L
- Toxic Criteria for those States Not Complying with Clean Water Act Section 303(c)(2)(B) criterion concentration for priority toxic pollutants:
  – Freshwater: maximum = 1.4 :ug/L, continuous = 0.77 :ug/L
  - Saltwater: maximum = 1.80 :ug/L, continuous = 0.94 :ug/L
  – Human health consumption = 0.3 mg/kg MeHg in fish tissue (wet weight).
- Water Quality Guidance for the Great Lakes System—protection of aquatic life in ambient water:
  – Acute water quality criteria for mercury total recoverable: maximum = 1.694 ug/L
  – Chronic water quality criteria for mercury total recoverable: continuous = 0.908 ug/L
  – Water quality criteria for protection of human health, drinking water and nondrinking water: maximum = 1.8E-03 ug/L
  – Water quality criteria for protection of human health (mercury including methylmercury) = 1.3E-03 ug/L.
- Listed as a hazardous air pollutant under Section 112 of the Clean Air Act
- Emissions from mercury ore processing facilities and mercury chlor-alkali plants = 2,300 ug maximum/24 h
- Emissions from sludge incineration plants, sludge drying plants, or a combination of these that process wastewater treatment plant sludge = 3,200 ug maximum/24 h
- Ban of phenylmercuric acetate as a fungicide in interior and exterior latex paints
- Reportable quantities: Mercury, mercuric cyanide = 1 lb; mercuric nitrate, mercuric sulfate, mercuric thiocyanate, mercurous nitrate, mercury fulminate = 10 lb; phenylmercuric acetate = 100 lb.
- Listed as a hazardous substance: Mercuric cyanide, mercuric nitrate, mercuric sulfate, mercuric thiocyanate, mercurous nitrate
- Reporting threshold for Toxic Release Inventory (proposed) = 10 lb
- Maximum Achievable Control Technology standard for waste incinerators = 5ug/dscm

2.0   SOURCES OF MERCURY IN THE ENVIRONMENT

Mercury is emitted into the atmosphere by both anthropogenic and natural processes. Because of its chemical properties, mercury is believed to change form and species as it is transported through the environment. Scientists have conceptualized this movement as a cycle.

Numerous researchers have studied the mercury cycle and as more is learned about mercury in the environment, the cycle is refined. Still, the current level of understanding fosters confidence only in general terms.

Based on our present level of understanding, the *Mercury Report to Congress* (USEPA, 1997b) suggested that the flux of mercury from the atmosphere to a location on the earth's surface was comprised of contributions from:

·   The natural global cycle;
·   The global cycle perturbed by human activities;
·   Regional sources; and
·   Local sources.

Fitzgerald (Fitzgerald, 1994) estimated that 5E+09 g or roughly 5,500 tons of mercury are in the global atmosphere. While attempts have been made to estimate pre-industrial mercury concentrations (i.e., before anthropogenic emissions were a part in the global cycle), it has proved difficult as mercury is continuously cycling through the environment. The Expert Panel on Mercury Atmospheric Processes (Expert Panel, 1994) estimated that pre-industrial atmospheric concentrations represent about one-third of the current mercury concentration in the atmosphere. Analysis of Swedish lake sediments (1994) showed mercury concentrations in the upper layers to be two to five times higher than those from pre-industrial times. Similar studies have shown increases as well. While it is accepted that atmospheric mercury concentrations have increased substantially since the pre-industrial period, it is not known whether overall atmospheric mercury levels are currently increasing, decreasing, or holding steady. Preliminary results (Grigal, 2002) for eastern red cedar growing near industrial sources showed peak mercury concentrations in wood formed in the 1950s and 1960s with stable or decreasing concentrations in the past decade. Some lake sediment core studies have shown that peak mercury deposition occurred prior to 1970 and may now be decreasing.

Schuster (Schuster, et al., 2002) provides an interesting discussion on the trends of atmospheric deposition over the last 270 years. The research is based upon analysis of mercury levels in glacial ice cores from the Upper Fremont Glacier in the Wind River Range of Wyoming. The layering of ice could be traced to specific years (similar to growth rings on a tree). Three mercury emissions from three major volcanic events (Tambora, Krakatau, and Mount St. Helens) were identified in the ice cores. However, the effects of mercury deposition from these events created mercury signals of fairly short duration (1-2 years); indicating that volcanic activity does not account for long term mercury concentrations in air. This study also looked at mercury emissions related to anthropogenic sources, and specifically mercury emissions associated with gold mining operations. Specific spikes in mercury were observed that can be correlated to the California gold rush; however, the increased levels of mercury are again short-lived and mercury levels quickly were at pre-industrial or background levels. The conclusion regarding natural sources of mercury (volcanic and mining) were that while individual events led to high short term deposition rates, the brief duration of the events limit their importance in overall mercury deposition. Rather, results from the cores indicate that during the last 100 years, anthropogenic sources contributed to 70% of total mercury input. Recently, a decline in mercury concentration in ice cores has been observed. Several factors have been identified as possible contributors for the decline in

concentration; however, the declines coincide with emission reduction controls under the Clean Air Act.

The downward trend in environmental mercury concentrations resulting from these and other studies generally is correlated to regional mercury use and consumption patterns over the same time frame. Thus, the studies do not establish a definitive decrease in the overall atmospheric mercury burden.

Mason (Mason et al., 1994) estimated that about half of total anthropogenic mercury emissions eventually enter the global atmospheric cycle; the remainder is removed through local and/or regional cycles. An estimated 5 to 10% of primary divalent mercury (Hg(II)) emissions are deposited within 100 kilometers of the emission point. Emitted elemental mercury (Hg^0) may be removed on a local and regional scale to the extent that which is oxidized to Hg(II). Some Hg^0 is taken up directly by foliage and most of the un-oxidized Hg^0 undergoes long-range transport due to its insolubility in water. In general, primary Hg(II) emissions are deposited locally or regionally depending on the degree that wet deposition processes remove the soluble Hg(II). Dry deposition may also remove some atmospheric Hg(II). The quantity of mercury deposited varies depending on source characteristics, the species of mercury emitted, meteorological and topographical attributes, and other factors.

Some additional air emission references should be consulted by the interested reader: (Lyman, S. et al., 2007), (Nacht, D. et al., 2004), (Seigneur, C. et al., 2004), and (Themelis, N., 2005).

2.1 Natural Sources

Volcanic activity, geothermal activity, and natural cinnabar deposits are obvious natural sources. Transport and conversion of the mercury to different forms from these sources is also natural and can occur anywhere on the planet. Even the arctic has been speculated to be a natural source of reactive gaseous mercury (Betts, K., 2001). To fully determine the source of a mercury contamination problem, both natural and anthropogenic sources need to be considered. However, identification of possible anthropogenic sources of heavy metals can be masked by the presence of natural sources. For example, Siegel (Siegel, B., et. el., 1984) collected samples of Equisetum arvense plants at multiple locations around Mount St. Helens in the two years following the major volcanic eruption in May 1980. Cycling of mercury showed a 10-fold to 73-fold increase of mercury in the plants from June 1981 through July 1982. One of the largest increases was in the City of Portland, which was particularly surprising given its distance and up-wind direction from Mount St. Helens. This natural source would certainly mask determination of anthropogenic sources of mercury in the Portland area.

Utah's geology is abundant with evidence of historical volcanic activity in many areas. Natural geothermal sources are also abundant in the State, as can be seen in the map available at: http://geology.utah.gov/geothermal/interactive/index.html. Mercury data on any of Utah's geothermal springs could not be located, however, the geothermal springs

in nearby Yellowstone Park contained up to 600 ng/L mercury. King (King. S., et.al., 2006) and other researchers used ultra-clean sampling methods and approaches typically used in pristine environments to quantify concentrations of Hg species in water and microbial biomass from hot springs of Yellowstone National Park. Total Hg, monomethylated Hg, pH, temperature, and other parameters influential to Hg speciation and microbial ecology were determined for hot springs water and associated microbial mats. Several hot springs indicated the presence of methylated mercury in microbial mats with concentrations ranging from 1 to 10 ng/g (dry weight). Concentrations of total mercury in mats ranged from 4.9 to 120,000 ng/g (dry weight). Combined data from surveys of geothermal water, lakes, and streams show that aqueous total concentrations ranged from l to 600 ng L^{-1}. Species and concentrations of total Hg in mats and water varied significantly between hot springs.

Although no fish consumption advisories were issued for Yellowstone, it is entirely feasible for high levels of mercury in geothermal sources to enter waters where fish receptors might be consumed.

(Please note that this protocol does not consider groundwater or geothermal water as a source of mercury, unless the groundwater or geothermal water has a pathway to biological receptors. As such, those waters would be considered springs and the protocol would cover them under surface waters).

A study of the Cache Creek, CA watershed is available (Domagalski J., et al., 2003) (http://www.sfei.org/watersheds/presentations/SPLWG/SPLWG_july2003_Item4.pdf) that showed contributions of thermal spring mercury were significant (up to 100 ppm). The authors also looked at other natural sources including naturally enriched Hg soils in the area and background Hg soil. They showed how this mercury and mercury from mining in the area plus global mercury sources must be considered together to understand the fate of mercury in a given watershed. One particular slide was particularly useful to this discussion and is presented in Figure 2-1.

Geologists have looked for natural mercury in soil to find mercury "hot spots" that successfully indicated faults or geothermal activity (Rasmussen, P., 1995). (http://ces.iisc.ernet.in/hpg/envis/mondoc1712.html).

Others have monitored mercury vapor over soil to successfully locate mercury contamination underground at a nuclear submarine base in Bangor, WA. (USEPA, 1993) (http://www.epa.gov/superfund/sites/rods/fulltext/r1093071.pdf). The same concept would work for finding faults or geothermal activity.

Geologic activity also causes natural release of mercury vapor. A news article from the Billings Gazette, Billings MT was released in 2003 that claimed scientists measured major mercury emissions in Yellowstone Park, that made them think their equipment was broken (http://ff.org/centers/csspp/library/co2weekly/2005-08-11/mercury.htm). At Roaring Mountain, scientists measured mercury emanating from the clay hillside at up to

2,400 nanograms per square meter per hour, significantly higher than measurements of 200-700 at other sites in the Norris-Mammoth corridor. By comparison, background levels away from geothermal areas range from zero to 10. They speculated the natural mercury emissions in Yellowstone might be more than all the coal-fired generating plants in Wyoming. If places like Yellowstone contribute significant amounts of mercury to the air, then regulations on man-made sources may not be as effective as once thought. More study on Yellowstone mercury emission is expected by scientists at the Idaho National Engineering and Environmental Laboratory (INEEL), and USGS.

Figure 2-1. Sources and Fate of Mercury in a Watershed.
(Domagalski J., et al., 2003)
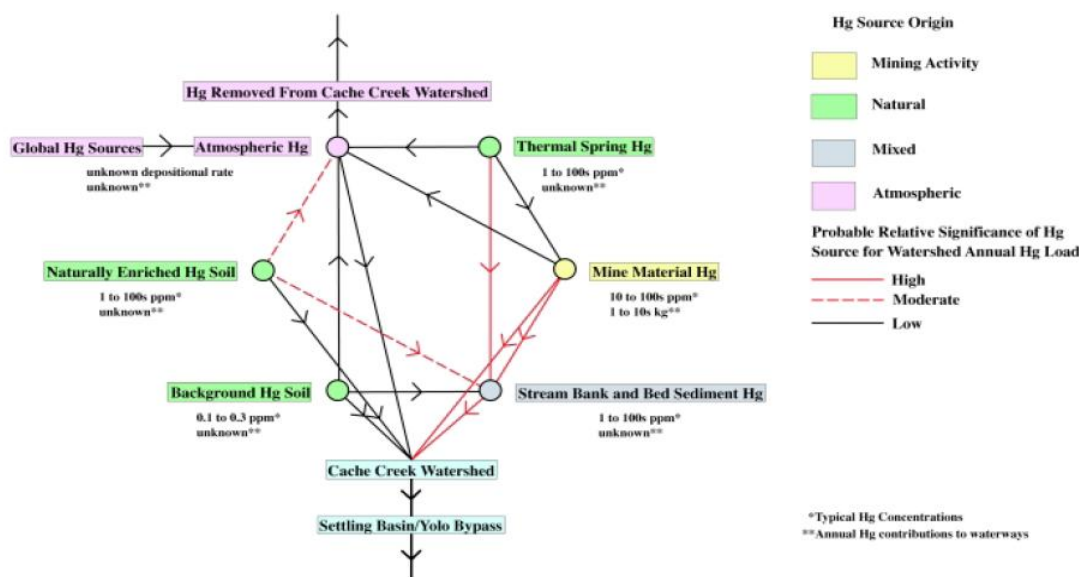
2.2 Anthropogenic Sources

The extent to which anthropogenic releases of mercury from mining, agriculture, or other land uses have contributed the mercury levels in fish is the principal objective of this study. A scientifically valid model for the dispersal and availability of mercury to aquatic receptors in surface waters of Utah is necessary to allow for decisions about the impacts of economic development.

Mercury can enter the environment from a variety of anthropogenic or manmade sources. These sources include the following:

- Combustion of coal in coal-fired power plants,

- Municipal waste incinerators, hospitals and crematoriums, dental offices,
- Thermal treatment of gold and mercury ores,
- Releases of mercury from current and legacy mining operations, and
- Geothermal heat recovery processes,
- Munitions Operations

Lesser known generators of mercury in the environment include crematoriums, dental offices and munitions operations. The following links will provide more information to the interested reader. Dental: http://www.epa.gov/region5/mercury/dentaloptions3.pdf, and http://www.epa.gov/glnpo/toxteam/potwp2.htm#110
Munitions: http://science.utah.gov/CAC/documents/jan18_2001minutes.pdf, and http://www.miltoxproj.org/munitions_and_ranges.htm.

As noted in Figure 2-2, below, the single primary contributor for U.S. emissions of mercury into the atmosphere is through coal boilers associated with utility/power plants. Most of the contributors including gold mines, hazardous waste incinerators, chlorine production facilities, and institutional boilers have remained fairly steady though the 90's, with the exception of medical waste incinerators and municipal waste combustors which have significantly reduced their mercury output.

Figure 2-2. U.S. Emissions of Human Caused Mercury. (USEPA, 1999 and UDEQ, 2006b)
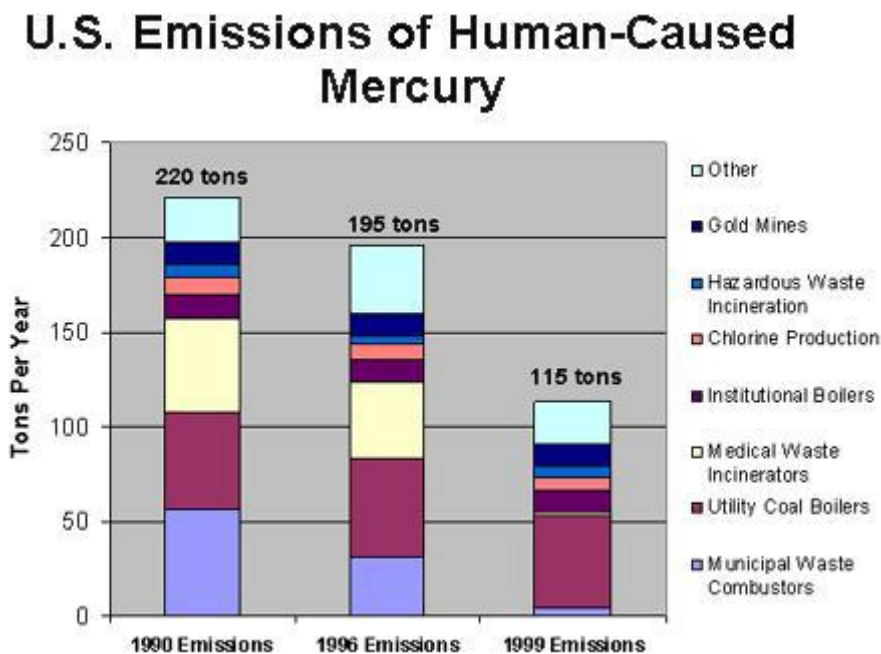
Understanding the impact of mining on the current mercury contamination levels in the State of Utah is of particular concern due to the large concentration of mining operations in the State and upwind of the watersheds where fish consumption advisories have been issued. There are thousands of abandoned gold mines west of the State of Utah in Nevada and California which is far too many to evaluate individually for their impact on the environment or determine source contamination. "Legacy Mining", is the term describing the past mining practices of these abandoned mines. In the mining of gold, legacy mining practices most frequently used elemental mercury or "quicksilver" to collect fine particles of gold from the ore, which was then recovered by a thermal process that vaporized the mercury into the atmosphere leaving the gold behind. This is no longer an acceptable practice, but how much damage has it done, and is damage still continuing from leftover mercury? Is mercury still vaporizing from the waste and tailings piles that remain at the sites, and how can that be evaluated?

To begin to answer those questions, or rule out legacy mining as a source of mercury contamination in Utah, it would be prudent to visit geographical areas that have a high concentration of legacy mining sites that are in the watershed or upwind from affected mercury contamination hot spots in Utah. Monitoring mercury levels in the air in those geographical areas is recommended. During times of air stagnation or low wind conditions, a mobile monitoring team such as that which is operated by USGS (see http://toxics.usgs.gov/highlights/usgs_mml_impact.html) could tour legacy mining hotspots in southern Nevada, California, and Utah and sample air just downwind from multiple sites. Similar efforts have been already conducted in Nevada between 1996 and 2003 and should be reviewed prior to expending resources in Utah (Gustin et al., 1996, Gustin et al., 2003).

If any hits are seen, the lab could attempt to take more samples in the area and pinpoint the source. A sampling plan should be developed to include the routes which get in close proximity to legacy mining sites for air monitoring. A sampling team would need to be observant for current small mining operations, and ensure that they collect air monitoring data in the vicinity of those mines. If no mercury is detected in proximity to large concentrations of legacy mines, there would be no chance for mercury vapor to affect Utah farther downwind, and that particular collection of legacy mines could be ruled out as mercury sources.

Media other than air, may be sampled from obvious waste areas of any legacy mine site if access is available to the sampling staff. These media (soil, sediment, water, fish) can be evaluated following the analytical protocols described elsewhere in this document to determine if legacy sites are still contributing to contamination in a given watershed. The following links show legacy mining sites in Nevada, California, and Utah. They clearly show, by virtue of the large number of sites, that legacy mines must be considered as potential mercury sources for contamination in Utah.

CA Abandoned Mines: http://www.earthworksaction.org/pubs/CA_AML_303d.pdf
NV Abandoned Mines: http://www.earthworksaction.org/pubs/NV_AML_303d.pdf
UT Abandoned Mines: http://www.earthworksaction.org/pubs/UT_AML_303d.pdf

In addition, the Utah Division of Oil, Gas, and Mining maintains a database of abandoned mines in Utah. The database is regularly updated and covers most areas of the state, although some gaps exist. The database does not contain information regarding the commodity mined, but limited information on the size, quantities mined, and area disturbed is available. See: http://www.ogm.utah.gov/amr/default.htm.

Once mercury is emitted into the atmosphere, the following processes are involved in the atmospheric fate and transport of mercury:

·   Emissions to the atmosphere;
·   Transformation and transport in the atmosphere;
·   Deposition from the air to the surface; and
·   Re-emission to the atmosphere.

Figure 2-3 illustrates how mercury emitted from a utility plant or a mining operation enters the atmosphere. The process outlined in Figure 2-3 is similar for most anthropogenic sources. Influencing factors on mercury once emitted from a source include: the form of mercury emitted, the location of the source, the height of the source (e.g., stack height or surface runoff from mining activities), surrounding terrain (flat versus mountainous), and weather conditions.

Figure 2-3. Behavior of Mercury Emissions. (http://www.epa.gov/mercury/ exposure.htm**)**
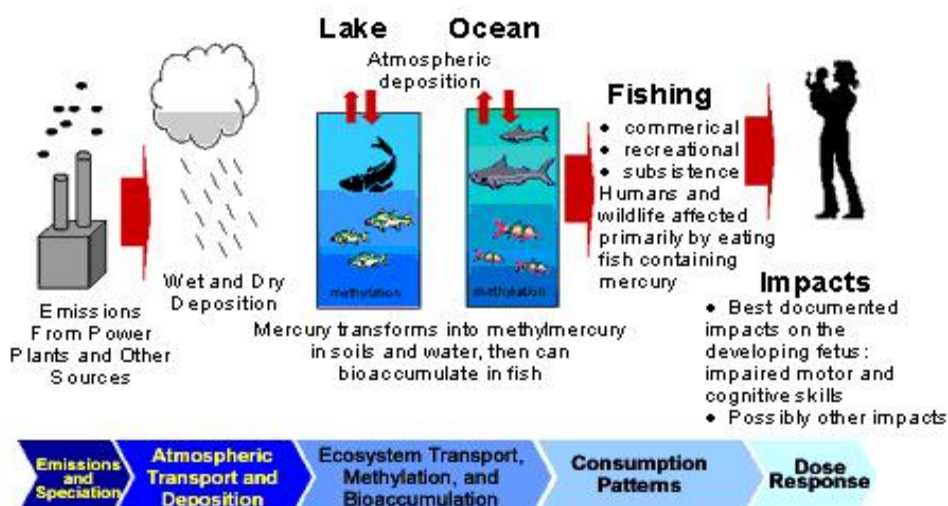
3.0   MERCURY INTERACTIONS

Mercury enters the atmosphere through naturally occurring and anthropogenic processes. Natural processes include volatilization of mercury in marine and aquatic environments, volatilization from vegetation, degassing of geologic materials such as soils, and volcanic emissions. Anthropogenic mercury releases are believed to be dominated by industrial processes and combustion sources. Stack emissions are thought to include both gaseous and particulate forms of mercury. Emitted gaseous mercury is thought to include both elemental and oxidized chemical forms while particulate mercury emissions are thought to be composed primarily of oxidized compounds. In addition, chemical reactions will likely occur within the emission plume. The speciation of mercury emissions is believed to be a function of the fuel used, and the design and operation of the flue gas cleaning equipment. The emitted stream is believed to range from almost all divalent mercury to nearly all elemental mercury with the divalent faction split between gaseous and particle bound phases (Lindqvist et al., 1991). Much of the divalent fraction is thought to be $HgCl_2$ (Michigan Environmental Science Board, 1993).

Once in the atmosphere, the mercury is transported, dependent on climatic conditions. The mercury then falls out via wet and dry deposition. Deposition, in general, refers to the transfer of airborne pollutants to the earth's surface where they either react with or adhere to some surface and thus, are removed from the atmosphere. Dry deposition is typically defined as the settling of gases and particles out of the atmosphere. Dry deposition of acidic constituents is commonly referred to as acid rain. Wet deposition is the process by which chemicals are removed from the atmosphere and deposited on the Earth's surface via rain, sleet, snow, cloudwater, and fog. Wet deposition involves the absorption of pollutants, both particles and gases, into liquid droplets or ice crystals. These pollutants are transferred, in most cases, to the surface in the form of precipitation. Wet deposition is also commonly referred to as precipitation scavenging, wet removal, rainout, and washout; however, wet deposition is not limited to precipitation. It also includes the deposition that occurs when low lying fog or haze droplets come into contact with a surface such as plant life or natural and man-made structures (APTI, 2006).

3.1   Mercury Transformation and Transport

Hg^0 remains in the atmosphere for up to one year and, thus, is fairly evenly distributed in the troposphere (http://pubs.acs.org/subscribe/journals/esthag-w/2004/oct/science/rr_rethinking.html). Hg(II) may be deposited relatively quickly by wet and dry deposition processes, thus, atmospheric residence times are estimated as hours to months. Longer residence times are possible; however. Porcella (Porcella et al., 1994) showed that the atmospheric residence time for some Hg(II) associated with fine particles may approach that of Hg^0.

The transformation of Hg^0(g) to Hg(II)aq and Hg(II)p in cloud water demonstrates a possible mechanism by which natural and anthropogenic sources of Hg^0 in air can result in mercury deposition to land and water. This deposition can occur far from the source due to the slow rate of Hg^0(g) uptake in cloud water. Fitzgerald (Fitzgerald, 1994) and

Lindqvist (Lindqvist et al., 1991) have suggested that this mechanism is important in a global sense for mercury. Gaseous divalent mercury is expected to deposit at a faster rate after release than particulate divalent mercury assuming that most of the particulate matter is less than 1 μm in diameter. According to Lindqvist and Rodhe (Lindqvist and Rodhe, 1985), an atmospheric residence time of ½ to 2 years for elemental mercury compared to one on an hourly scale for some divalent mercury species is expected. This disparity in atmospheric residence time between Hg^0 and other mercury species leads to larger scales of transport and deposition for Hg^0. Generally, air emission of Hg^0 from anthropogenic sources, fluxes of Hg^0 from contaminated soils and water bodies, and natural fluxes of Hg^0, all contribute to a global atmospheric "reservoir" with a holding time of ½ to 2 years. Emissions of all other forms of mercury are likely to be deposited to the earth's surface before they are entrained into the "global atmosphere".

3.2   Deposition of Mercury

Researchers believe that gaseous elemental mercury, Hg^0, is the most abundant species in the atmosphere and, due to its relatively low solubility in water, exhibits the longest residence time. The divalent species are manifested as particle-bound mercury, HgP, and reactive gaseous mercury, RGM. RGM is comprised of gaseous species of oxidized mercury and is highly soluble in water; thus, its residence time in the atmosphere can be relatively short. Atmospheric residence time for HgP is characterized as intermediate.

Both HgP and RGM are assumed to dry deposit (defined as deposition in the absence of precipitation) at significant rates when (and where) measurable concentrations exist. The deposition velocity of HgP is dependent on atmospheric conditions and particle size. Particulate mercury is also assumed to be subject to wet deposition due to scavenging by cloud microphysics and precipitation. Both HgP and RGM have much lower Henry's Law constants than Hg^0, and are assumed to partition strongly to the water phase. Dry deposition of RGM is believed to be significant due to its reactivity with surface material. As a result of its reactivity and water solubility, RGM is more rapidly and effectively removed by both dry and wet deposition than HgP (Lindberg et al., 1992; Petersen et al., 1995; Shannon and Voldner, 1994).

In contrast, Hg^0 is not thought to be susceptible to any major process of direct deposition to the earth's surface due to its relatively high vapor pressure and low water solubility. There does appear to be potential for deposition of elemental mercury via plant-leaf uptake; however. Hanson (Hanson et al., 1994) showed that a downward flux of elemental mercury from the atmosphere occurs resulting in a deposition velocity when air concentrations of elemental mercury are above an equilibrium level for the local forest ecosystem. At lower air concentrations levels, the forest acts as a source of elemental mercury and emits back to the atmosphere. On regional and global scales, dry deposition of elemental mercury does not appear to be a significant pathway for removal of atmospheric mercury.

However, it is possible for elemental mercury vapor in the atmosphere to be deposited to the earth's surface. Chemical reactions occur in the cloud droplets that both oxidize elemental mercury to divalent mercury and reduce the divalent mercury to elemental mercury. The most important reactions in this aqueous reduction-oxidation balance are believed to be oxidation of elemental mercury with ozone, reduction of divalent mercury by sulfite ions (SO_3^{-2}), or complexation of divalent mercury with soot to form particulate divalent mercury:

- $Hg^0(g) \rightarrow Hg^0(aq)$
- $Hg^0(aq) + O_3(aq) \rightarrow Hg(II)(aq)$
- $Hg(II)(aq) + soot/possible\ evaporation \rightarrow Hg^0(aq)$

The Hg(II) produced from oxidation of Hg^0 by ozone can be reduced back to Hg^0 by sulfite; however, the oxidation of Hg^0 by ozone is a much faster reaction. Thus, a steady state concentration of Hg(II)(aq) is built up in the atmosphere and can be expressed as a function of the concentrations of $Hg^0(g)$, $O_3(g)$, H^+ (to represent acids), and $SO_2(g)$. The Hg(II)(aq) would then be susceptible to atmospheric removal via wet deposition. However, the third reaction may transform most of the Hg(II)(aq) into particulate form due to the much greater amounts of soot in the atmosphere compared to mercury. The resulting Hg(II)(p) can then be removed by wet deposition if the particle is still associated with the cloud droplet or dry deposition (following cloud droplet evaporation).

In summary, mercury released into the atmosphere deposits mainly as divalent mercury (i.e., HgP and RGM) from either direct deposition of emitted divalent mercury or from conversion of emitted elemental mercury to divalent mercury through ozone-mediated reduction. The former process may result in elevated deposition rates around atmospheric emission sources and the latter process results in regional and global transport followed by deposition.

3.3   Re-emission of Mercury to the Atmosphere

Re-emission of deposited mercury results most significantly from the evasion of elemental mercury from the oceans. In this process, anthropogenically emitted mercury is deposited to the oceans as Hg(II) and then reduced to volatile Hg(0) and re-emitted. As discussed above, mercury also cycles and recycles between the atmosphere and the earth's surface. Re-emission due to forest fires can also be a significant source (http://www.sciencedaily.com/releases/2007/10/071017131817.htm)

3.4   Transportation Other than in Atmosphere

Both atmospheric and hydrological processes contribute to the transportation of mercury in the environment. The accumulation of mercury in fish results from direct deposition of mercury from the atmosphere onto surface waters and watersheds as well as

contributions from hydrologic pathways. Hydrologic pathways and sources of mercury include direct discharge of wastewater, accidental releases of mercury-contaminated wastes into the environment, and the erosion and transport of naturally occurring geologic sources and mining residues by surface waters.

One study (Boudou, A., et al., 2005) presented the results of a comparative study of mercury in the water and fish of two adjacent rivers in French Guiana, with and without gold mining activities. The mined river with higher suspended particulate matter showed significantly higher total mercury concentrations in unfiltered water samples. Surprisingly, no significant differences were observed in mercury concentrations between 13 common fish species at upstream sites. However, mercury concentrations in fish caught downstream from a hydroelectric reservoir, where the two rivers flow, was up to 8-fold higher than that upstream. Mercury speciation measurements showed that these mercury differences in fish were related to the water distribution of monomethylmercury. The dissolved compound levels were low and similar in both rivers, while they were 10 times higher in the water outflowing the hydroelectric dam. Dissolved monomethylmercury determinations along a water column profile suggested that methylation of inorganic mercury happens in the depths of the reservoir under anoxic conditions. The authors conclude that mercury mobilization related to gold mining is not solely sufficient to account for high concentrations in fish and that environmental conditions that favor mercury methylation, such as anoxia, are needed.

That anoxia is implicated in mercury methylation, may address why waterfowl in the Great Salt Lake have elevated mercury levels. One reviewer of this protocol speculated that the high levels of methyl mercury in the lake are due to anoxic brine created by a salinity differential on either side of an artificial causeway. That may well be the causative factor, rather than a high mercury input.

Some additional references might be consulted by the interested reader, which include (Mohapatra, S. et al., 2007), and (Ullrich, S. et al., 2001).

Figure 3-1 shows the transportation of mercury once deposition has occurred and shows how mercury interacts between soil, water, sediment, and ecological receptors.

3.5   Methylation of Mercury

Mercury enters the ecosystem via direct deposition onto drainages, lakes/streams and onto soil. Erosion of soil also contributes to the increase in mercury into various water bodies. Bacteria in soil and sediments convert mercury into methylmercury. Methylmercury is easily taken up by aquatic plants and animals and may be converted into more complex organo-mercury compounds. As larger organisms feed on these smaller organisms, methylmercury is concentrated up the food chain in a process called bioaccumulation. In general, methylated mercury is ingested by algae (phytoplankton). These algae are in turn consumed by shellfish and zooplankton. Small foraging fish eat

Figure 3-1. Flow Diagram of Mercury (Hg) Transport to Surface Water.
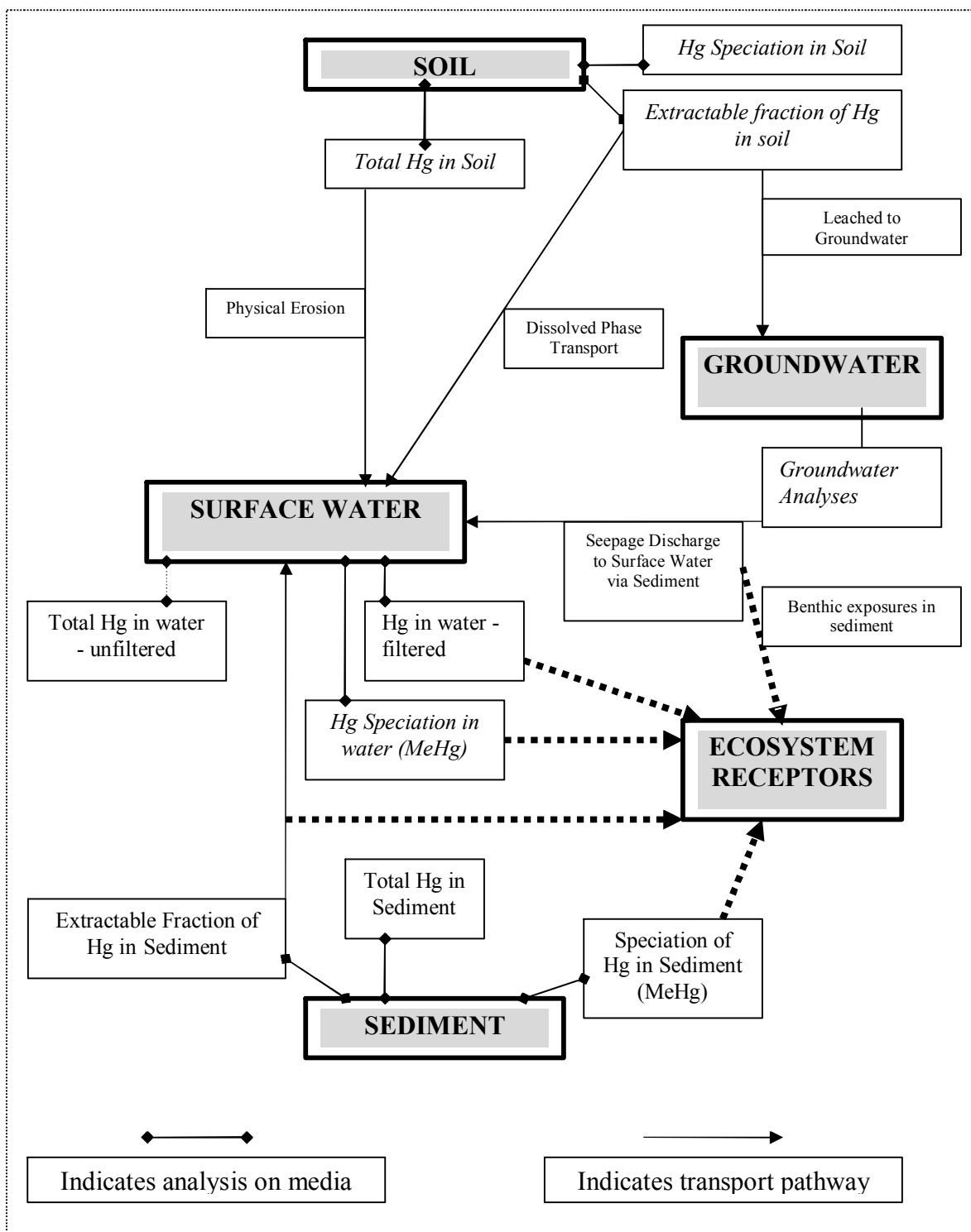
the shellfish and zooplankton. Predatory fish, such as bass and trout, prey on the small foraging fish. Humans and large game in turn consume the larger predatory fish.

For example, one study (Kuwabara, J., et al., 2007) studied mercury speciation in predatory fish from legacy mining areas. Guadalupe Reservoir in California, and Lahontan Reservoir in Nevada, are both affected by mercury from mining and have advisories for fish consumption, per USEPA guidelines. Replicate X-ray absorption near edge structure (XANES) analyses on largemouth bass and hybrid striped bass were performed. Despite significant differences in mercury source, the proximity of the source, and concentrations of complexing ligands, results of XANES analysis clearly indicated that mercury accumulated in these individual fish from the two reservoirs were dominated by methylmercury cysteine complexes. These findings agree with results from commercial fish species inhabiting marine environments which are presumed to include differing mercury sources (e.g., atmospheric, hydrothermal, or benthic). The dominance of methylmercury cysteine complexes in muscle tissues of fish obtained from significantly different environments and exposure conditions suggests that a generic toxicological model for the consumption of fish could be applicable over a wide range of ecologic settings. USGS (USGS, 2006) (http://pubs.usgs.gov/ds/2006/151/) discusses methods to study methylation and demethylation rates of sediments. Although the data would be useful for this protocol to generate, the expense may be outside the scope of this study.

Figure 3-2 illustrates the process of methylation of mercury and how methylmercury becomes mobilized in the food chain. Methylmercury concentration in fish depends on many factors, including mercury speciation, concentration of mercury in water, water pH and temperature, amount of dissolved solids and organic matter in water, and the organisms present in the ecosystem. Because of these factors, and due to the complexity of food webs, bioaccumulation can be difficult to predict and can vary widely from one water body to another.

Figure 3-2. Methylation of Mercury (USGS, 2000)
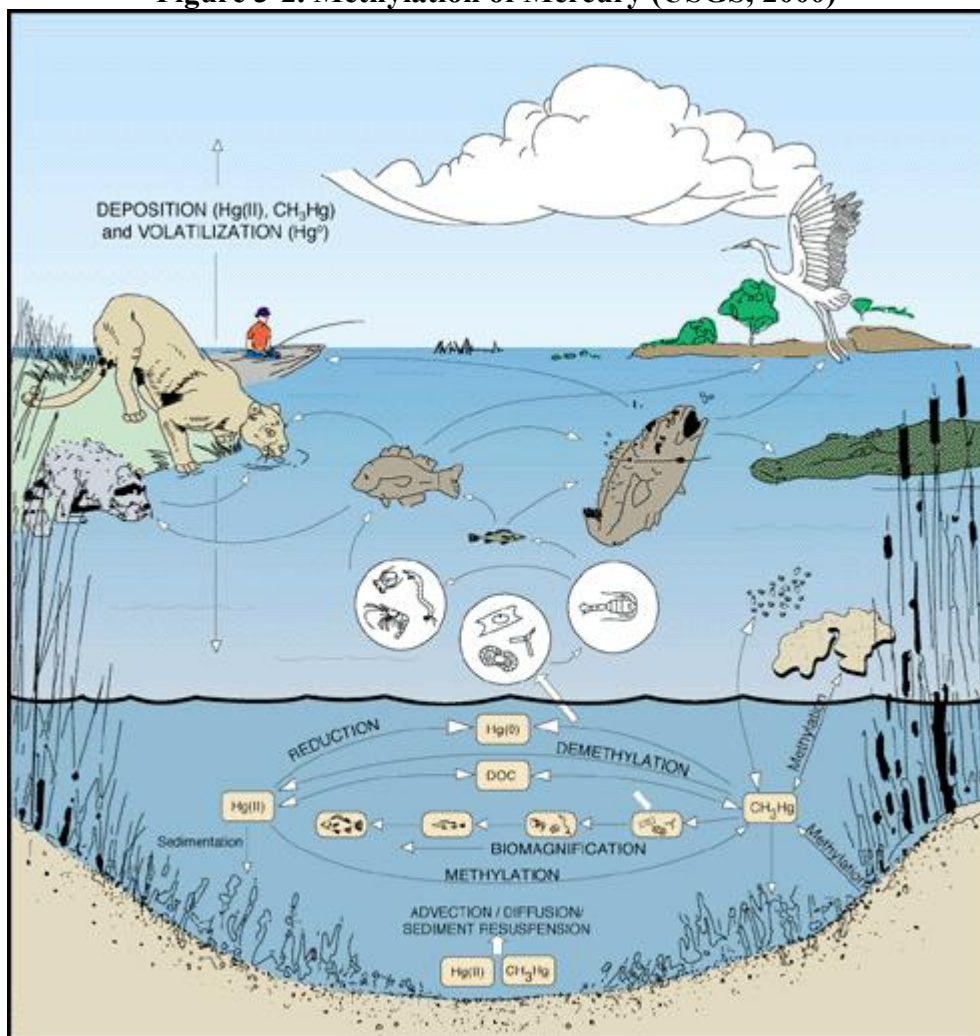
4.0   SOURCE ASSESSMENT (HOW TO USE THIS PROTOCOL)

The primary purpose of this protocol is to outline the approach Utah DEQ will take to assess the sources of mercury at locations where fish tissue data indicate mercury contamination is occurring. Currently, there is an understanding of mercury occurrence in various fish tissues sampled and analyzed across the State of Utah (Utah Department of Health [UDOH], 2007). This information identifies areas where mercury has accumulated and created possible human health concern. As a result, fish advisories have been issued in order to protect human receptors from possible harm as a result of contaminated fish tissue ingestion.

The next step towards addressing the concerns related to this condition, is to conduct a 'source area assessment' which serves to identify possible sources of mercury that have lead to the accumulated fish tissue concentrations. Since Utah DEQ already has a baseline set of information which identifies fish tissues with mercury, it is now possible to begin the first steps towards isolation of the concerns and possible source areas (rather than starting at the ground level, trying to identify where possible concerns lie). This protocol and the companion Quality Assurance Project Plan (QAPP) provide the independent pieces from which Utah DEQ can pick and choose for their development and implementation of sampling procedures. However, before these independent sampling or standard operating procedures can be applied, an overall conceptual plan and understanding of the source areas needs to be developed for each area of study.

This Section provides the proposed Phased protocol for developing area, or site-specific sampling strategies for a source assessment which was built upon the UDEQ 'Mercury Source Protocol Concept' (UDEQ, 2006a). The first step is to build a conceptual understanding of the possible source areas from available information (Phase 1 – Conceptual Model Development). Where 'data gaps' are identified, Phase 2, or Confirmation Sampling is completed in order to obtain area-specific information that will fill the data gaps and help isolate the nature and extent of the area of concern. Upon completion of Phase 2, the data obtained will help provide an Inventory of the Existing Site (Phase 3). This information should be sufficient to characterize the entire setting, otherwise it may be necessary for the researchers to go back to Phase 2. Eventually (depending on funding), each independent occurrence of mercury could have a comprehensive data-substantiated conceptual pathway leading back to the source that created the condition (Phase 4). Upon completion of all the Phases, the process of source area control or reduction can begin. However, as shown above, these Phases are iterative and dependent upon the data outcomes and ability to be interpreted. The results may not be straight-forward and several cycles of repeated Phases may be required. The following subsections provide a narrative description of the overall protocol approach as summarized above and shown in Figure 4-1. The protocol users are free to choose their 'starting point' which is dictated by the amount of information available for the setting being evaluated. The remainder of this protocol and the companion QAPP provide the distinct, independent protocols for very specific field programs (e.g. moss sampling). This information is provided for the protocol users to be used as per their discretion and applicability to their site being evaluated.

Figure 4-1. Protocol Flow Diagram

Phase 1 - Conceptual Model Development

Desk-Top Source Area Assessment

- Delineate area of study or watershed
- Gather existing info from previous studies
- Gather info on possible natural sources
- Gather info on possible anthropogenic sources
- Plot wind rose patterns, GW flows, SW flows
- Identify data gaps
- Map available data
- Make observations for spatial trends in maps of air, sediment, surface water, snow pack, biota, and soil data

Documentation of the Conceptual Model For the Study Area

Use Figure 4.2 as a template to tentatively identify source areas, fate and transport pathways, and possible affected media.

See example in Figure 4.3. Can now focus on sources, release mechanisms, and receptors that weren't eliminated.

Phase 2 - Confirmation Sampling

Revisit Utah DEQ Fish Data Set

- See if it is spatially or temporarily representative of current conditions.
- Review it's 'robustness'
- Determine if watershed was adequately captured

Create a spatial map of proposed sampling efforts to correct data gaps

Prepare a broad, general characterizing sampling plan

Perform sampling using biased sampling and composite samples of affected media

Perform analyses using methodology in Section 5 for affected media

Confirm mercury problems that still exist, eliminate areas requiring further study

Phase 3 - Inventory of an Existing Condition

Refine sampling plan to be more definitive for affected media

Within scope of available budget, perform specific sampling and focused analyses using methodology in Section 5 and QAPP

Evaluate and identify mercury sources

Phase 4 - Source Area Monitoring

For areas subject to methylated mercury problems, set up monitoring programs to monitor mercury over time

Collect samples and perform recommended methods in Section 5 and QAPP under schedule in monitoring program

Review data for temporal changes

Make recommendations for remediation or control of problem

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4.1 Phase 1: Conceptual Model Development

The first step is to assess whether elevated levels of mercury are present and if so, in what media are they elevated. Using these data, a conceptual model of where mercury contamination is present and the areas of elevated contamination can be mapped. In addition, trends and/or spatial variations may become visible with more data. The relationships between data may be used to help identify whether the elevated levels of mercury are due to a non-point source, are naturally elevated levels, or may be traced to a specific point source. Areas requiring more detailed focus and/or characterization can be identified. Additional sampling can then be focused on these hot spots. Using this tiered approach will allow for minimization of costs and allow for focus to be placed on identified media and sources of concern.

Utah DEQ has addressed this first step with the state-wide evaluation of mercury occurrence in various fish tissues (UDOH, 2007). This information has been compiled and interpreted in order to identify areas of concern. As a result of these investigations, a baseline understanding of mercury occurrence has been gathered. Thus, the process of focusing on specific areas, or watersheds with mercury concerns can begin. The approach to identify source areas will rely upon this initial information derived by Utah DEQ. The next steps will rely upon the researchers obtaining area-specific or watershed-specific information in order to derive a Conceptual Model.

General Conceptual Models depicting mercury behavior were previously shown in Figures 3-1 and 3-2. At this Phase of the protocol process, a more specific Conceptual Model will be developed based upon a 'desk top' evaluation of possible source areas to a specific area of concern. The following subsection describes the methods by which available documents, internet-based information sources etc., can be compiled to formulate a basic understanding of the possible source areas. Once the source areas are identified, the area-specific Conceptual Model can be formulated. These two tools will then guide the researchers towards the next steps within the Protocol for the development of a Confirmation Sampling Plan (Phase 2).

4.1.1 Desk-Top Source Area Assessment

A desk top approach is recommended as the first step towards a source area assessment for an area known to contain fish tissue mercury issues. A desk-top approach means that existing information gathered by historic investigations will be relied upon. The ultimate goal of the effort is to gain a cursory understanding of the possible sources of mercury, pathways of transport, and affected receptors; which are known in these cases to be fish with the measured concentrations of mercury. Figure 4-2 depicts a general conceptual model with the certain building blocks of various pathways that can connect mercury sources to receptors. Results of this desk-top step will identify those applicable blocks or pathways and lead to the development of an area-specific Conceptual Model. It may be found that information is lacking and these pathways are largely unknown. If this is the case (which is likely at this Phase), then the researchers will proceed to Phase 2.

Figure 4-2. Example Ecosystem Conceptual Model
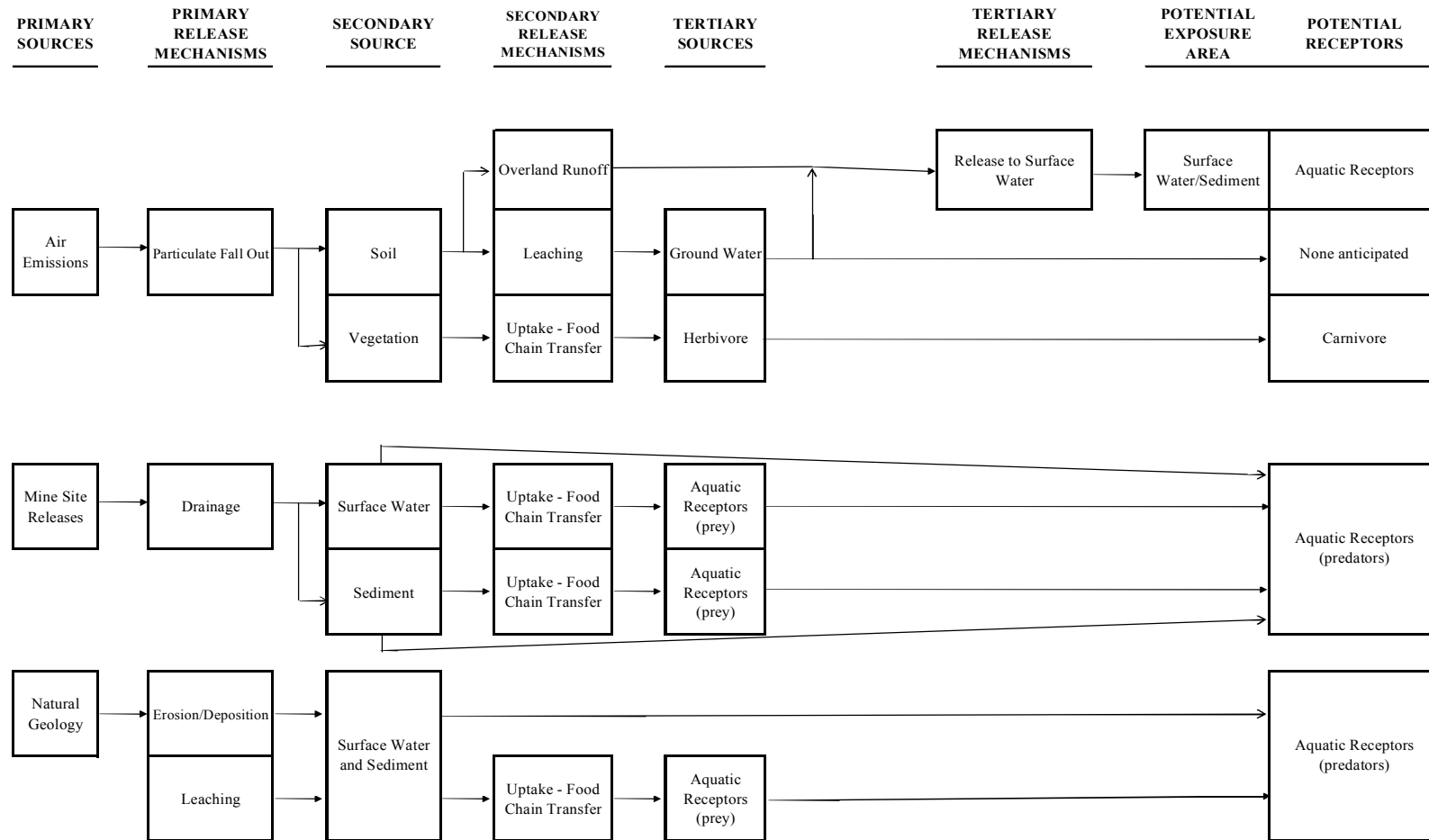
The recommended steps within this component of Phase 1 are as follows;

a) Delineate the area of study using a watershed approach. Delineate the area using the watershed concept of topographic high points representing the outer-most boundaries, and cumulative perennial drainage outfalls as the lowest boundaries (already delineated within the UDOH, 2007 documentation). Delineate areas immediately adjacent that may contain possible mercury source areas as well.

b) Gather existing information from previous studies that characterize mercury content in both abiotic (non-living) and biotic (living) components of the area of study. Collect information of areas immediately adjacent as well, if there is the possibility of any transport connective pathways (air, groundwater). Use all available information from various sources [academic literature, previous Utah DEQ studies, Utah DWQ studies, (http://www.waterquality.utah.gov/Monitoring/2007_dwq_Monitoring_plan.pdf)USGS studies, abandoned mines database, STORET, CERCLA, and RCRS databases, etc.]. USGS has compiled data on general levels of Hg throughout the United States. The data show Utah has relatively low levels of mercury among the western states. The following two links provide more information: http://tin.er.usgs.gov/geochem/, and http://tin.er.usgs.gov/geochem/map/image/lower48/hg_aa.jpg

c) Gather information that describes all possible natural sources of mercury from a spatial perspective by obtaining maps of soils and geologic formations. Research the possible mercury content and yield associated with these media (refer to Section 2.1 of this protocol) for the watershed area, as well as adjacent watersheds.

d) Gather information that describes all the possible anthropogenic (man-made) sources of mercury from a spatial perspective by obtaining maps of mining activity, power plants, industrial activities, National Pollutant Discharge permits with mercury as a regulated release, etc (refer to Section 2.2 of this protocol) for the watershed area, as well as adjacent watersheds.

e) Plot wind-rose patterns, groundwater flow pathways and surface water pathways within the watershed study area, as well as adjacent watersheds to establish possible connective pathways between source areas and watershed components.

f) Identify data gaps from the information gained above. Review the information obtained from a critical perspective of temporal and spatial quality. It may be found that information is too historic, or gathered and analyzed for purposes unsuitable for these studies etc.. The results may be too uncertain to gain useful information from and represent a data gap in the understanding of the area setting.

Sources for mercury in the environment can be linked to either a point source or a non-point source from either anthropogenic or natural sources. Point sources would include a specific industrial facility, such as a utility plant, incinerator, or other operation. Non-

point sources include naturally occurring mercury in soil and global fallout. Identifying the specific source for mercury contamination appears to be a difficult task. The question at hand is "is it possible to evaluate media-specific data and determine the potential source for the mercury contamination?"

One approach considered was to see if specific industrial processes left a traceable signature on mercury. Based upon a review of available literature, it does not appear that specific signatures can be detected on the sampled mercury that would allow tracing back to a specific facility. In discussions with Dr. Robert Taylor, Texas A&M University Dept. of Veterinary Integrative Biosciences, similar studies have been conducted in Texas to determine whether specific facility processes left any type of imprint or signature on mercury that would allow tracing the mercury to a specific facility. While several studies were conducted, no successful means of tracking mercury were found. Dr. Taylor mainly attributed this to the physical and chemical properties of mercury (conversation, November 2006). Thus at this time, the identification of the source(s) for mercury may be dependent on the evaluation of the spatial distribution of mercury.

The first step in identifying the potential source(s) for the mercury (as part of the Conceptual Model for a given area of study) would be to map the available data for all media historically sampled. By mapping the data, spatial trends may become visible. By evaluating the data, observations such as the following may be observed for each medium. Results of media analysis provide a first indication of affected media, and possibly source media. The following describes how various media can be used to spatially interpret possible mercury source areas.

- Air: Based upon literature review, mercury emissions into the air appear to be the driving factor in elevated concentrations of mercury in the environment. Surveying Utah for the types of facilities that historically emit mercury into the air and identifying their area of potential mercury deposition based on weather patterns is a recommended starting point. Existing data from surrounding states, as well as mercury modeling studies similar to those described in Section 4.2, should be reviewed to identify potential sources located beyond Utah's borders. The location of areas impacted by the identified sources can be refined through a comprehensive air modeling analysis of mercury emissions. Once the potential deposition areas within the State are identified locations could be selected outside those areas where background or global mercury fallout in Utah can be measured. Comparing those background/ global deposition measurements to elevated data collected near potential point sources coupled with air modeling results for those sources, could identify whether emissions are emanating from the point source and whether the emissions are being transported to sensitive area(s) of concern.

- Sediment: Sediment data will provide an indication of transport and mobilization of mercury. However, it appears that unless there is an identifiable source in soil, sediment data will not be useful in identifying a point source.

- Surface Water: Using surface water data to identify a point source or non-point source for mercury appears to be difficult. For streams, comparison of up gradient and down gradient data should be compared. In addition, any sediment data and soil data should be reviewed to see if there are any localized areas with greater contamination. It may be possible to trace higher levels to erosion of soil into the stream. For lakes, the data for the inlet and outlet as well as near the center of the lake should be compared. This will allow some correlation as to whether there is a significant influx of mercury from streams flowing into the water body. Water quality measurements should be compared to air data. If there is a spike/change in water quality there may be a correlation with higher than usual air emissions, which could be traced to a facility emission. It may be possible to develop a crude mercury balance table weighing the air emissions data with the sediment, soil, and snowpack data.

- Snow Pack: Data results from snow pack analyses will provide information on both global fallout but will also reflective of industrial emissions. The data alone will not be useful to pinpoint a particular source, but when coupled with the data from the air monitoring program, trends may be visible that will allow for a "separation" of global emissions versus those emissions from an industrial source. The data should be evaluated in conjunction with meteorology data, such as predominant wind direction.

- Biota: Fish and invertebrates are not a plausible source for mercury but rather are indicator species of mercury contamination. Therefore, the data from biota sampling will only point to levels of contamination and not be useful in identifying a possible source for the mercury contamination. If the results from the biota analyses are consistent within species, a conclusion may be drawn that adequate characterization samples have been collected. However, if there are uneven trends within species, additional characterization may be required. In addition, if data from a specific species sampled is consistently higher than other species, this species may be more sensitive to mercury and may be useful as an indicator species. Additional sampling may be warranted to confirm any conclusions.

- Soil: If the mercury concentrations are uniformly distributed in soil, then it is likely that mercury in soil is the result of a combination of naturally occurring mercury and to some extent global fallout. If there are pockets of higher concentrations, these areas should be marked for further investigation. Additional sampling may be necessary to verify whether the localized hot spots are a result of a different type of geology or whether the area has been impacted by an industrial/mining process.

4.1.2   Documentation of the Conceptual Model

The information gathered from the previous subsection can be used to begin filling in the Conceptual Model for the area of study. Using Figure 4-2 as a template, the researchers can begin to tentatively identify the source areas, the fate and transport pathways and possible media affected by mercury. It will be likely that sources, pathways and affected media are 'unknown' and should be highlighted as such. An example of a conceptual model developed for an area with the following information is shown in Figure 4-3.

- Mercury in edible game fish tissues (bass) occurred at concentrations above the EPA threshold of 0.3 mg/kg. Mercury was not detected in composite surface water samples co-located with the fish tissues. Sediment samples were not collected.

- Research indicates the presence of historic mining activities using mercury-amalgamated process up-gradient from the fish sampling locations and also occur in the adjacent watersheds.

- Ground water occurs at least 500' below ground surface and does not communicate with surface water bodies.

- The drainage occurs within a shale formation known to have ambient mercury content. The adjacent watershed occurs within a separate non-mercury containing geologic formation.

- There are no air-emission sources within the watershed, but it is unknown if there are possible sources in adjacent watersheds.

Results of the above information, when plotted on the example Conceptual Model (Figure 4-3) highlight the possible pathways needing confirmation through the process of confirmation sampling in Phase 2. Results from sampling of various media related to these pathways will help confirm the presence/absence of mercury source areas. Some key concepts to consider using the above conditions as an example:

- Bass are predators and can obtain mercury exposure through a variety of exposure pathways. It would be important to understand if prey species contain mercury concentrations that can accumulate into the bass tissues, in addition to other exposure media such as surface water and sediment.

- An understanding of 'ambient' or 'background' mercury contributions as related to the geology can be tested by comparison of soils/geologic samples from the area of study as compared to the adjacent watershed.

- Air emissions is an unknown for the adjacent watershed. Similar sampling approaches should be designed for both settings to obtain unbiased general characterizing data sets.

- Sampling locations that 'bracket' the possible mining sources such as samples obtained 'above, within and below' the source would help determine if the mine(s) are sources.

4.2 Phase 2: Confirmation Sampling

Phase 1 set the stage for the protocol by gathering all available information using a desk top approach. This information, when boiled down into a Conceptual Model for the area of study, serves to highlight those pathways (and affected media) requiring further study. Phase 1 is important from the perspective that it gathers all available information thereby eliminating the possibility of completing duplicate investigations, and by effectively focusing the next steps which involve sampling. Sampling is expensive and time consuming and should be focused as much as possible before embarking upon even a broad-scale confirmation approach such as described within this Phase.

Phase 2 is referred to as 'Confirmation Sampling' because it confirms the presence of the already detected mercury in the fish tissue data set obtained by Utah DEQ. As described within the Utah DEQ Mercury Assessment Protocol Concept (UDEQ, 2006a), confirmation sampling serves to evaluate 'adjacent waterbodies for mercury in fish tissue and evaluate additional species of fish in the waterbody of focus (area of study). It is important to confirm the presence (or absence) of the mercury condition since temporal and spatial variables may have been introduced since the initial fish tissue collection event. At this Phase, it is also recommended that data gaps identified from Phase 1 also be pursued from a 'grand scale' meaning a broad brush or even biased approach in order to determine if whole pathways are even present. For instance, from the example cited at the end of subsection 5.1, air emission pathways are a 'potential' pathway from the adjacent watershed. This is an 'unknown' condition thereby representing a data gap that could be addressed by further study of the possible air emission sources, and/or some soil or moss sampling.For the purposes of the Phase 2 Confirmation Sampling this protocol proposes the following steps;

a) Revisit the existing Utah DEQ fish tissue data set to determine if it is spatially, and temporarily representative of current conditions. Also review the dataset from a 'robustness' perspective. Are there other species present that are important (e.g. game fish or game fish present) that were not sampled, and should be to confirm the presence of mercury within the fish exposure pathway. Revisit the data set to determine if the watershed for the area of study was adequately captured. Similarly, review the data set from the perspective of adequacy for the adjacent watershed.

Figure 4-3. Case Example Conceptual Model

PRIMARY SOURCES	PRIMARY RELEASE MECHANISMS	SECONDARY SOURCE	SECONDARY RELEASE MECHANISMS	TERTIARY SOURCES	TERTIARY RELEASE MECHANISMS	POTENTIAL EXPOSURE AREA	POTENTIAL RECEPTORS
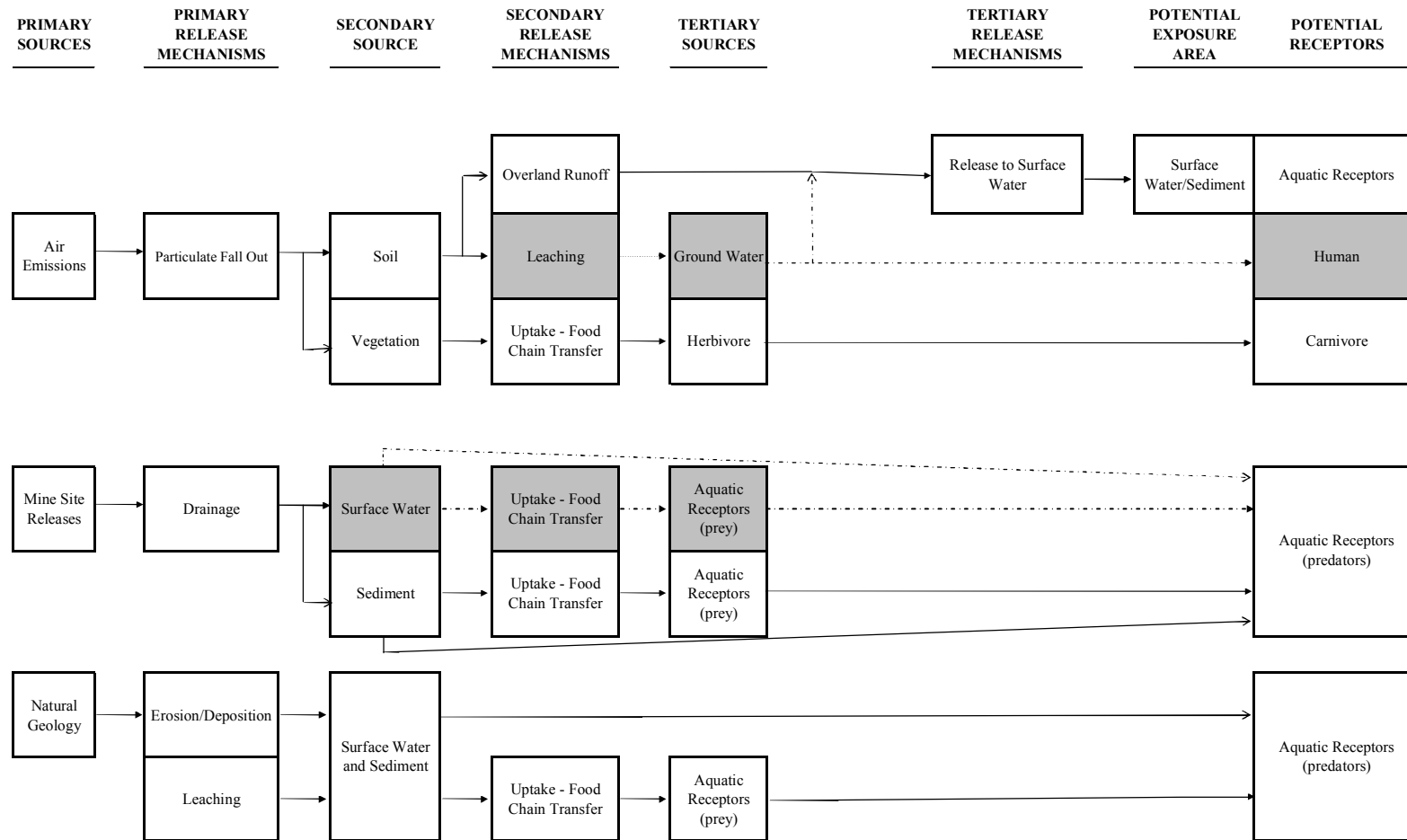
Shaded boxes and dashed lines indicate incomplete or insignificant pathways.

b) Create a spatial map of proposed sampling efforts to correct data gaps identified from Phase 1. Revisit these data gaps and the needs from the previous step regarding fish confirmation sampling to determine how to stream-line the approach and gather enough information to be able to 'confirm' the presence of mercury.

It is important to recognize that this Phase is strictly confirmatory in nature. It is not a scientific endeavor to delineate source areas. This Phase of sampling is strictly cursory to answer yes or no questions regarding; the presence/absence of mercury in fish tissue within the watershed that captures the area of study, and within adjacent watersheds; to confirm or deny the presence of mercury in various sources, pathways or affected media that are unknown as a result of Phase 1 findings.

Broad, general characterizing type sampling strategies should be applied at this Phase. This would include the collection of composites over large areas, the collection of representative species (not already collected) etc. Recommendations for sampling strategies during this Phase include;

- Biased sampling of affected media within and immediately adjacent to possible source areas (e.g. surface water and sediment above within and below a mine release, or soils within known area of air emission fall out) to answer definitive questions about possible sources, pathways and affected media.

- Composite samples of abiotic media over broad areas that have unknown sources to detect the presence/absence of mercury and be able to eliminate whole portions of the area of study for later definitive source area delineation.

- Composite samples of fish tissues by species by stream segment or lake to determine if various food chain pathways are complete or incomplete. Samples of bottom dwellers will help to determine the completeness of sediment to fish, samples of pelagic fish will help determine the completeness of surface water to fish etc..

The number of samples to be collected should be few. There is no statistical objective associated with this Phase. The results will provide only broad conclusions to serve as the foundation of the more definitive source area delineation studies to be designed in forthcoming Phases. Phase 2 will identify 'existing conditions' or specific site settings that contain mercury and require further source area assessment within Phase 3 and possibly Phase 4.

4.3   Phase 3: Inventory of an Existing Condition

Results of Phase 2 served several purposes; it confirmed the presence of mercury in fish tissues within and adjacent to the area of study, and pursued to address broad data gaps identified in Phase 1. The results may serve to eliminate areas requiring further study due to the lack of detected mercury, and also served to identify additional areas requiring further study. Phase 3 represents the Phase where source areas can become the focus of the sampling program. It is up to the professional discretion of the researchers however, to determine the applicability of each Phase to their unique area of study.

Phase 3 differs from Phase 2 in that is it more 'definitive' and should be designed to be of high quality with concepts of quality assurance/quality control and statistical relevance being integrated into the overall design. The goal is to identify or prove that sources of mercury exist. As such, the data need to be defensible and robust. Phases 1 and 2 are intended to have focused the sampling program on only those areas, pathways and affected media of known concern, and broad questions regarding the area setting will have been addressed.

It is important to apply concepts of data quality objectives (as described within Section 5.1) for this Phase. Each sampling activity should have a clear objective with stated data quality goals. At the summation of the field events and data analysis, the goals should be revisited to be sure they were achieved. At times, field or laboratory error will affect the goals. If the effect is negligible, then the data is still of sound quality. If the effect is insurmountable, a data gap and additional efforts need to be put forward to fix the error.

Each media-specific protocol provided in Section 5 describes the proposed sampling approach from a spatial perspective, number of samples and type of analysis to conduct. The companion QAPP provides details regarding the available equipment that can be used and further detail in regards to actual sample collection. Both the protocol and QAPP strongly endorse the completion of a 'site reconnaissance' prior to the design of any field investigation effort since site conditions of access, habitat etc. will affect sampling outcome. The protocols in Section 5 and within the QAPP are general guidelines designed to provide a robust, and statistically (or spatially) sound data set. It is always up to the professional discretion of the researcher to determine their applicability within a specific area of study.

Using the example begun in subsection 4.1 and demonstrated on Figure 4-2, the potential Phase 3 components for this field design would involve protocol steps for air deposition as described in Section 5.2, sediment in Section 5.3 and fish and invertebrate sampling (Section 5.6). If weather conditions permit, the approaches for sampling snow pack (Section 5.5) would also apply. The approaches provided within these independent protocols, when combined with the QAPP will provide sufficient information for Phase 3. Results of Phase 3 will delineate the source areas but may only capture a 'snapshot in time'. Mercury is very dynamic in the environment and through the process of

methylation can become more problematic over time. It is possible that the Phase 3 efforts will capture only a temporary condition of the mercury and not depict the methylated potential. For those areas of study found to have definable source areas releasing to settings conducive for methylation (refer to discussion in Sections 1 and 2), implementation of Phase 4 is recommended. Phase 4 encompasses sampling associated specifically with the source areas using a monitoring approach. This entails repeated sampling at similar locations of media historically collected from previous Phases in order to observe change over time. Results will provide an indication of the methylation potential and persistence in the environment.

4.4   Phase 4: Source Area Monitoring

Phase 4 is implemented upon completion of previous Phases that clearly define the mercury source areas. Once the source areas are understood, it should be possible to identify the media that contain mercury concentrations to provide a clear indication of source area releases. These indicator media should be monitored over time in order to understand the temporal (and potential spatial) changes in mercury. Mercury can become more problematic through the methylation process, or environmental processes can sequester and abate mercury. At this Phase, the indicator media (which can be abiotic or biotic) should be sampled over time and analyzed for methylated forms. The frequency of sampling is related to the 'release rate' of the source, flow conditions or hydrodynamics of the water body, and seasonal influences. Monitoring should capture typical conditions throughout the year. It may be best to capture at least high and low flow settings. It may be more prudent to capture a sampling event once per quarter especially if sampling includes the capture/analysis of biota with seasonal life stages. Enough data should be gathered to isolate the variables affecting the mercury to understand when conditions change and in response to what variables. This may entail several years of data collection. The results will be used to determine when 'best' and worst case conditions occur. This helps to design the controls to put in place to ensure best release rates for the source area.

Phase 4 sampling efforts can also rely upon the protocols provided within Section 5 and the companion QAPP. However at this Phase, sampling will be extremely focused. At the very least the following conditions should be static;

- The sampling locations that provide the best data from which to compare year-to year (or season to season) changes should be located using the global postioning system, mapped and relied upon at each sampling event.

- Other measures of variables that can affect the amount of mercury in the samples (such as flow) should be routinely collected in order to be able to isolate the variables affecting mercury.

- The same suite of analysis and same types of samples should be captured at each sampling event. Consistency is an element of QA/QC and is essential to

monitoring programs. If possible, retain the same field personnel, and laboratory for all field and analytical work.

- The numbers of samples collected is dependent upon the use of the data. Statistical robustness may no longer be a requirement. Biased or non-random sampling may be appropriate.

5.0   MEDIA SPECIFIC SAMPLING

The broad objective of this study is to determine how wide spread mercury contamination is in Utah. Following a tiered approach, the initial step is to develop a conceptual model to evaluate naturally occurring (baseline) mercury levels and the effects of anthropogenic loading of mercury in various media. Results from the initial characterization will allow for a more refined and focused assessment on the predominant media of concern.

Based upon a review of literature the following media have been identified as being important in determining levels of mercury in the environment as well as for aiding in the identification of the potential source(s) for mercury:

> Air,
> Sediment,
> Surface water,
> Snow pack,
> Biota, and
> Soil.

Groundwater would not typically be a significant contributor to surface water and biota contamination unless there is a direct source of mercury contamination above the groundwater body (e.g., a spill, leaking storage tank, etc.). Therefore, unless site-specific conditions warrant, groundwater sampling is not recommended as necessary for the initial characterization/investigation (refer to previous discussion presented in Section 4).

5.1   Considerations Prior to Implementing a Sampling Program

Optimizing a sampling and analysis plan prior to field implementation will allow for the most cost effective program and result in useful data. The first step is the planning process or development of Data Quality Objectives (DQOs). The basic steps in the DQO process (shown in Figure 4-1) are:

- Define the problem that needs to be addressed;
- Define possible decisions;
- Define the data input and associated activities;
- Define the boundaries of the study;
- Develop decision rules;
- Specify the limits on decision error; and
- Optimize the sample design.

The optimization and design process may be an iterative process of selection and re-evaluation of design alternatives to determine the most resource-effective design that meets the DQOs (ASTM, 1998).

Figure 5-1. DQO Process.

Define the problem that needs to be addressed

↓

Define possible decisions

↓

Define the data input and associated activities

↓

Define the boundaries of the study

↓

Develop decision rules

↓

Specify the limits on decision error

↓

Optimize the sample design
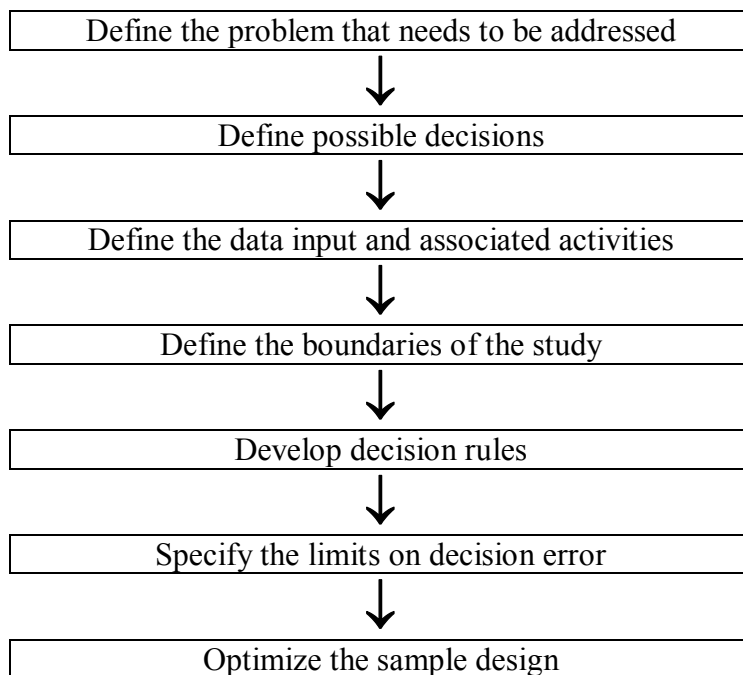
The seven steps of the DQO process are discussed below.

Step One: State the Problem

The problem is the situation that needs to be investigated or investigated further. The problem is determined based on the conceptual site model developed at the beginning of the site characterization using known information about the site. The conceptual site model may include the location of known areas of elevated mercury or potential contaminant sources, types of contaminants expected, types of media potentially contaminated (e.g., soil, surface water, air, etc.), potential migration pathways, and potential human and ecological targets or receptors. The output from Step One may be a simple statement that describes the contamination problem or potential contamination problem that may present a threat or unacceptable risk to human health and the environment. Step One should be repeated and new outputs developed as the site enters into different phases of the site characterization (WDEQ, 2005).

Step Two: Identify the Decision

Identifying the decision is basically stating the possible decision(s) that will address the problem. Several decisions may be necessary to address the problem; therefore, more than one statement may be included in this step. For example, a decision may be identified to determine whether or not concentrations of contaminants are present above the mercury advisory level or above average background concentrations.

Step Three: Identify Inputs to the Decision

This step identifies the information that will be needed to support the decision(s) identified in Step Two. Types of information that may be required will depend on the site and the information already available. Some types of information that may be needed include physical soil and surface water data, chemical data, historical data, and action levels. The output from Step Three is a list of information inputs required to resolve the decision statement (WDEQ, 2005).

Step Four: Define the Boundaries of the Study

This step defines spatial (physical and geographical), temporal (time periods), demographic, and regulatory boundaries for the investigation. Identified during this process are the area(s) and depth to be investigated, the media to be investigated (e.g., surface soil, air, biota, surface water, or sediment), the timeframe of the investigation, and the potential population (human, plant, animal) that could be affected. This step also defines the practical constraints that could interfere with the investigation. For sites where little to no environmental information is already available, the boundaries of the study may not be easy to define. The boundaries of the study may therefore either expand or be reduced as more information about the site is obtained (WDEQ, 2005).

Step Five: Develop a Decision Rule

The decision rule is a logical "if...then" statement that describes the rule for taking certain actions in response to the findings of the investigation. The rule is most commonly applied to action and/or cleanup levels and the action taken if the action levels are exceeded.

Step Six: Specify Tolerable Limits on Decision Errors

This step establishes the degree of uncertainty (decision errors) that is acceptable to the decision makers. Because it is impossible to sample an entire medium being investigated, the samples collected and the corresponding analytical results must be deemed representative of the medium of concern. The potential for error increases when few samples are used to characterize a large area or volume. For example, if a sample represents a large area of soil and the soil sample has mercury concentrations exceeding an action level, the entire area represented by the sample will be considered contaminated. If not all of the soil represented by the sample is contaminated, some soil may be unnecessarily deemed elevated. If no contaminants are detected in a sample, the entire area represented by the sample will be considered clean and a decision to not remediate that area may be made. If some soil represented by the sample is actually contaminated, contamination that should be evaluated may be left in place. The more samples that are collected, the more likely the concentrations recorded can be used to accurately represent conditions in the area and the likelihood of an incorrect decision is decreased. The limit of uncertainty that is acceptable, therefore, may be driven by the risks to human health and the environment and the potential remediation cost. The

acceptable limit of uncertainty will provide a framework for the sampling design (WDEQ, 2005).

Per USEPA (1989), the DQOs should be established prior to the collection of data. DQOs are predicated in accordance with the anticipated end uses of the data which are to be collected. DQOs are applicable to all phases and aspects of the data collection process including site investigation, design, construction, and remedy operations. It is important to note that the level of detail and data quality needed will vary with the intended use of the data (USEPA, 2001).

Prior to the initiation of any data collection activity, a site-specific Sampling and Analysis Plan (SAP) should be prepared. This SAP should include data-specific DQOs and address the following:

- Logically evaluate available site information;
- Specify site-specific Measurement Quality Objectives for precision, accuracy and completeness for each parameter being measured;
- Select an appropriate sampling design;
- Select and utilize suitable geophysical, analytical screening, and sampling techniques;
- Employ proper sample collection and preservation techniques;
- Collect and analyze appropriate quality assurance/quality control (QA/QC) samples;
- Logically present and interpret analytical and geophysical data; and,
- Define data usability criteria.

DQOs associated with analytical results are typically assessed by evaluating PARCC (Precision, Accuracy, Representativeness, Completeness, and Comparability) of all aspects of the data collection process. PARCC is defined as:

- Precision; a measure of the reproducibility of analyses under a given set of conditions.
- Accuracy; a measure of the bias that exists in a measurement system.
- Representativeness; the degree sampling data accurately and precisely depict selected characteristics.
- Completeness; the measure of the amount of valid data obtained from a measurement system compared to the amount that was expected to be obtained under "normal" conditions.
- Comparability; the degree of confidence with which one data set can be compared to another (USEPA, 2001b).

More specific details on the DQOs, SAP, and QA/QC procedures are outlined in Appendices A and B.

5.1.1   Sample Design

Several types of sampling designs may be used including Authoritative, Simple Random, Stratified Random, and Systematic. However, as the purpose of this study is to determine whether elevated levels of mercury are present and if so, identify the possible source(s) for the mercury, Authoritative sampling is proposed. This type of sampling design is based upon subjective judgment and is one of the most cost effective sampling designs. However, a draw back to this type of sampling approach exists. No objective probability of selection is assigned to any of the units in the population, so there is considerable uncertainty in estimating sample variance of the population (ASTM, 1998).

Once the first tier of characterization has been completed and hot spots identified, a more refined approach, using systematic sampling may be appropriate. Systematic sampling is useful in evaluating hot spots and trends.

Numbers of samples for each medium addressed in this protocol have been discussed. For prescribing sampling designs, such as simple random or random stratified, there are methods available that can be used to calculate the number of samples required to meet DQOs. Examples of these calculation methods are outlined in ASTM (1999). However, for initial characterization using authoritative sampling, calculation of samples is not a requirement. Rather, the numbers are based upon judgment. Numbers of samples will vary based upon the size of the area under investigation. However, the sections below do provide some guidance as to the number of samples that should be collected for each medium.

5.1.2   Other Considerations

An important reminder for any sampling program employed is documentation of the sampling event and a system for re-location of the samples. For large scale projects such as those that may be implemented using this protocol, it is suggested that each sample location be marked using a global positioning system (GPS). This will allow for precise location of each sample result and will also allow for easier mapping and contouring of results.

Another problem encountered when sampling is that too little sample is collected to meet the requirements of the laboratory. Once the sampling program has been established, it is recommended that the laboratory be contacted to verify the amount of sample needed to perform the requested analyses for each medium being sampled.

The laboratory should also be contacted concerning holding times. While holding times are more critical when dealing with volatile organic compounds, holding times will need to be met to ensure compliance with the data quality objectives (DQOs). Since much of the sampling under this program may occur in more remote areas, packing and shipping of samples should be addressed prior to going into the field.

The Quality Assurance Project Plan (QAPP) and associated standard operating procedures (SOPs) provide more detailed information concerning developing project specific DQOs, a quality assurance program, sample collection, sample preservation, analytical tests, and chain-of-custody requirements. These are provided in Appendices A and B.

5.2   Air

Utah participates in the Western Regional Air Partnership, a voluntary organization of western states, tribes, and federal agencies and is a member of the Western States Air Resources Board. The Western Regional Air Partnership focuses on visibility issues while the Western States Air Resources Board offers a forum for all air quality issues. Both organizations are dedicated to improvements in air quality throughout the West and may provide an opportunity for networking and information exchange.

As summarized in Section 3.2, mercury in the atmosphere is deposited to the earth's surface by wet and dry processes. Depending on its form, and the conditions in the atmosphere, the deposited mercury can emanate from local, regional, or global sources.

Seigneur has applied a multiscale modeling system to study trends in the global fate and transport of atmospheric mercury over the contiguous United States. The research effort included a receptor location in the southwest corner of Colorado. At this location, Seigner reported mercury from anthropogenic sources in North, Central, and South America, Africa, Europe, and Asia with the most significant contribution (over 20% of the total mercury deposited from natural and anthropogenic sources) from Asian sources (Seigneur et al. 2004).

Wet deposition of mercury is monitored at nearly 90 Mercury Deposition Network (MDN) locations across North America. Currently, there are MDN monitoring sites in New Mexico and Nevada. An MDN site was added to the Utah Air Monitoring Center in January 2007. While atmospheric modeling and limited measurements indicate that dry deposition is an important mechanism for introducing mercury into an ecosystem, measurement of dry deposition of mercury is not yet routine and measurement data are not generally available.

Research teams in Northeastern North America (Miller et al., 2005), Nevada (Lyman et al., 2007), and New Mexico (Caldwell et al., 2006; Carr, 2006) are working to characterize dry deposition of mercury in their respective locations. In 2005, a team of researchers from Ecosystems Research Group, USEPA Region 1, the University of Michigan Air Quality Laboratory, the United States Geologic Survey (USGS), Environment Canada, the Vermont Agency of Natural Resources, and the Ministere de l'environnement du Quebec published the results of an estimation and mapping analysis of dry mercury deposition in northeastern North America (Miller et al., 2005). The study was conducted to gain knowledge of spatial patterns in mercury atmospheric deposition so as to better understand the risks to ecosystems stemming from this process.

Atmospheric mercury concentrations in aerosol, vapor, and liquid phases were obtained from four observation networks encompassing 27 measurement sites and used to estimate regional surface concentrations fields. The predicted patterns of total mercury deposition (the sum of precipitation-delivered mercury, $Hg^0(g)$ assimilation by vegetation, reactive gaseous mercury (RGM) and dry-aerosol deposition, and cloud droplet interception) were complex. Elevation, land cover, and proximity to urban areas all influenced the general pattern of deposition. The estimated net $Hg^0(g)$ and RGM fluxes (where RGM represented the sum of $HgCl_2$ and $HgBr_2$) were each greater than or equal to wet deposition in many areas.

In the study, total deposition spanned an order of magnitude from 3 to 30 $\mu g/(m^2 \cdot yr)$. The majority of deposition coincided with the growing season (late spring to early fall). The study team found that precipitation, RGM and $Hg^0(g)$ dry deposition each contributed about a third of the total estimated mercury deposition. In general, particle deposition represented less than 1% of the total. Cloud-water deposition was generally unimportant except for areas above 1000 meters in elevation. Precipitation tended to dominate total deposition in the non-forested areas considered in the study. Further, differences in surface conditions such as the presence or absence of forest and type of forest were found to influence the magnitude of the estimated dry deposition fluxes.

Based on their experience the researchers recommended establishing monitoring networks for wet and dry deposition including improvement of the existing networks. Issues related to size, standardization and stability were cited as deficiencies of the existing networks, preventing the reliable detection of regional-scale temporal trends. Further, establishing a mercury dry-deposition network was deemed essential because this study and others (Grigal, 2002) suggest that RGM and $Hg^0(g)$ deposition may represent from ½ to 2/3rds of total mercury deposition.

Another interesting project on dry deposition of mercury is ongoing in Nevada. Through an USEPA Local-Scale Air Toxics Ambient Monitoring Program Grant, the University of Nevada Reno (UNR), Frontier Geosciences, and the Nevada Division of Environmental Protection are conducting a study tasked with development of broadly-deployable methods for quantifying atmospheric mercury speciation in urban and rural settings (Carr, Power Point Presentation, 2006). As part of the study, researchers co-located field sites with urban and rural MDN sites and compared concentration and speciation of mercury measurements at urban and rural locations to develop a better understanding of the dry and wet deposition processes. Further, comparisons were made of data collected upwind and downwind of naturally enriched areas and potential anthropogenic sources.

The first phase of the work, focused on dry deposition, is nearing completion. Data on mercury speciation in air were examined to develop insight into the dry deposition of mercury in Reno and two rural MDN sites with the goal of measuring atmospheric mercury species and applying different techniques to infer dry deposition at the two Nevada MDN sites. UNR inferred dry deposition by:

· Deploying Surrogate Surfaces;

- Measuring Soil Flux;
- Determining deposition on Leaf Surfaces;
- Applying mathematical models to measurements of RGM and Hg(p); and
- Comparing all collected data to Wet Deposition MDN Data.

As expected, the researchers found that dry deposition rates depended on meteorological and surface parameters, as well as the composition of mercury species in the atmosphere. Further, each of the methods used showed that dry deposition was a significant component of total atmospheric mercury deposition. The different methods showed similar seasonal and geographical variations in the depositional behavior of Hg^0, RGM, and Hg(p), and each form of mercury was found to be a significant and even dominant component of total dry deposition at some sites and/or during some seasons.

Additional work is needed. RGM is the most reactive of atmospheric mercury species, has the shortest atmospheric residence time and is thought to have the highest deposition velocity; however, little is known about dry depositional behavior of both RGM and Hg^0.

Through laboratory testing, UNR is developing a diffusive sampler for RGM. Frontier Geosciences is developing a total mercury diffusive sampler that UNR will then test in a laboratory setting. The RGM diffusive samplers will be similar to the Surrogate Surfaces Sampler described earlier in that the collection surface is a filter that has high affinity for RGM and not elemental mercury. It is different in that the diffusive sampler collection surface is protected from atmospheric turbulence and, thus, collection to the filter should be linear relative to RGM air concentration.

Note that the diffusive sampler measures concentration, not deposition as atmospheric concentration is the most important predictor of depositional flux for RGM. The measured concentration can then be used for calculations related to deposition.

After laboratory testing is complete and units are ready, field testing will occur simultaneously with a Tekran 2537A Gaseous Mercury Analyzer fitted with a 1130 (RGM) and 1135 (Hg(p)) speciation unit and micro-meteorological and other routine ambient air quality parameters. Once initial field testing is complete, the researchers have proposed broad deployment at:

- Three MDN sites,
- A National Park Service air quality monitoring site,
- Transects down wind of a coal-fired power plant,
- Transects down wind of an ore-processing facility, and
- Transects down wind of a naturally enriched (geogenic) area

This final phase of field deployment will test the ability of personnel to obtain measurements of RGM on a broad scale, in remote locations, and with minimal training.

Ultimately, it is hoped that the project will collect data to advance the understanding of major research questions related to the biogeochemical cycle of mercury and determine if

source apportionment can be accomplished by measuring atmospheric speciation using passive sampling systems. Further, an understanding of how mercury speciation in urban air compares with that of air at remote sites and those downwind of known anthropogenic sources will be developed.

Researchers are also hoping to determine the significance of dry deposition of mercury relative to wet deposition especially in arid systems. Finally, since the dominant form of Hg in the atmosphere is Hg^0, the team will study the significance of dry deposition of Hg^0 relative to that for RGM or Hg(p).

The concentration and dry deposition of mercury species in an arid climate have been studied by Caldwell (Caldwell et al., 2006). In arid regions, precipitation is reduced and dry deposition becomes a more important component of total deposition. In this study concentrations of Hg^0, Hg(p), and RGM were measured and dry deposition was calculated via species-specific deposition velocities taken from Seigneur. Further, dry deposition was measured directly by ion exchange membrane for comparison to calculated values.

Caldwell reported that measured concentrations for all species agreed with other measurements made in North America and with modeled estimates. The researchers observed a diurnal pattern for RGM with the lowest values achieved at night. No discernible diurnal pattern was exhibited by Hg^0 and Hg(p). Seasonal effects were not observed in the measurements. Total deposition was estimated using 24-hour mean concentrations and wet deposition measurements obtained from MDN monitoring sites in New Mexico. Total deposition rates were reported as consistent with those associated with arid sites in remote locations in the absence of regional sources of mercury emissions. Further, Caldwell noted that dry deposition of Hg^0 represented both the largest and most uncertain fraction of total deposition and additional research was needed to better characterize this term.

Dry deposition measured with the ion exchange surface was greater than that obtained by calculation of dry deposition from concentration measurements. The particle collection efficiency of the ion exchange surface is not well understood and due to this uncertainty, no preference between the two methods for determining dry deposition flux was expressed by the researchers. Caldwell identified the major sources of uncertainty impacting the comparison as the deposition velocities used in the calculation method and the collection properties of the ion exchange membrane.

Other researchers (Mosbaek *et. al,* 1988) have reported some success with a potentially low-cost sampling method for mercury deposition. In a field experiment conducted by Carpi (Carpi et al., 1994) biological samplers were deployed around a modern municipal solid waste (MSW) incinerator. Sphagnum moss (*Sphagnum spp.*) and Italian ryegrass (*Lolium multiflorum Lam.*) were used as biological monitors of atmospheric mercury around a municipal solid waste incinerator in rural New Jersey. Moss and grass samples were exposed according to standardized techniques at sixteen sites within five kilometers of the incinerator. Background and quality control measurements were also made. In all

cases, mercury concentrations in moss exceeded those in grass. Mercury accumulation by moss exhibited a spatial pattern consistent with a local source of pollution, considering wind and precipitation. Total mercury in moss exposed at sites within 1.7 kilometers of the incinerator averaged 206 ppb while samples exposed at greater distances from the facility averaged 126 ppb.

Further analysis was performed by Opsomer (Opsomer et al., 1995) using the data from the moss samplers in modeling mercury deposition. The deposition of mercury around the incinerator site was modeled using a non-parametric technique, locally weighted least squares regression. The technique was applied to data on mercury accumulation in moss samples around the incinerator site, a situation where parametric modeling is not appropriate because of the small sample size and the presence of many potential covariates. The results suggested that the incinerator indeed impacted the spatial distribution of mercury in the immediate vicinity of the incinerator. Approximate F-tests indicate that the effect was statistically significant at the 10% level only after the moss samples have been oven-dried. A potential explanation for this finding based on the relative volatility of different mercury species was discussed.

5.2.1   Modeling the Atmospheric Deposition of Mercury

As discussed previously, atmospheric mercury exists primarily in elemental form but is also present in a variety of compounds. As mercury is transported around the globe, it reacts with other species in the atmosphere under the influence of meteorological conditions resulting in the continuous cycling of mercury to and from the atmosphere. At any point, at any time, these processes can be global, regional, and local in nature.

There are currently no widely accepted guidelines for mercury deposition modeling. Modeling approaches or protocols are formulated based on the specific situation that must be addressed. Some questions can be answered with a single model; others require a combination of modeling tools to achieve the desired result. For example, long range/regional impacts of local sources can be estimated using a regional scale model. Regional scale grid-based models can be used in combination with Gaussian models to estimate the contribution of various source types (e.g., anthropogenic, natural, Asian, neighboring states) to total mercury deposition over a given area. This combination of modeling tools allows for maximum flexibility in addressing a wide range of factors associated with mercury deposition, allowing the strengths inherent in one model to compensate for the weaknesses in another.

Regional scale grid-based models such as CMAQ, CAMx, and HYSPLIT are well suited for addressing the influences of multiple emissions sources on mercury deposition. They incorporate complex chemical mechanisms. Typically, their application requires the specification of boundary conditions by a global-scale model like GEOS-Chem. When effects smaller than the size of a grid cell need be resolved, point/non-point source Gaussian models such as the USEPA's AERMOD can be applied.

The five models identified above have been successfully applied in estimating mercury deposition. A brief description of each model is provided below. Note that numerous models are capable of estimating total mercury deposition. Selection of the appropriate model(s) should be based on the specific requirements of the analysis to be performed.

CMAQ

USEPA promotes the community Multiscale Air Quality (CMAQ) modeling system as best meeting the requirements of the Mercury Study Report to Congress recommendation for a "single air quality model" to address mercury deposition. The Agency used the model in performing the air quality modeling in support of the Clean Air Mercury Rule (USEPA, 2005b).

CMAQ is a three-dimensional grid-based Eulerian air quality model designed to estimate pollutant concentrations and depositions over large spatial scales (e.g., the contiguous United States). It accounts for spatial and temporal variations as well as differences in the reactivity of mercury emissions and appropriately accounts for the atmospheric reactions of specific mercury emissions and their significance in the levels of deposition. In addition, the boundary and initial species concentration are provided by the three-dimensional global atmospheric chemistry and transport model, GEOS-CHEM. CMAQ is a publicly available, peer-reviewed, state-of-the-science model consisting of a number of attributes that are critical for simulating the oxidant precursors and non-linear chemical relationships associated with the formation of mercury. Version 4.3 of CMAQ reflects updates to improve the science underlying the model and address peer review comments. Numerous updates to mercury chemistry are included.

The CMAQ model is designed to simulate the physical and chemical processes that govern the formation, transport, and deposition of gaseous and particulate species in the atmosphere. The CMAQ modeling system supports the detailed simulation of mercury (Hg), including the emission, chemical transformation, transport, and wet and dry deposition of elemental, divalent, and particulate forms of mercury.

At this point, it is difficult to assess model performance for total mercury deposition. Current beliefs, based on very limited measurements, are that wet and dry deposition are approximately equal in importance. Unfortunately, there is no measurement network for dry deposition of mercury (the MDN exists for wet deposition), so modeled predictions of dry deposition cannot be assessed against measurements. An analysis of model performance in predicting wet deposition showed that CMAQ, on average, underpredicted wet deposition.

CAMx

ENVIRON International Corporation's Comprehensive Air quality Model with extensions (CAMx) was modified to treat atmospheric processes for mercury. The mercury chemistry module implemented in CAMx was developed by Atmospheric & Environmental Research, Inc. and has been tested and evaluated (Seigneur et al., 2001).

Other implemented improvements include: refinements to the dry deposition module to better resolve differences between seasons and the effects of snow cover. The effect of snow cover on photolysis rates was also accounted for in the modified CAMx.

Boundary conditions are derived from a global mercury chemistry transport model (CTM). The CTM used in the Wisconsin study has been applied in numerous studies that investigated mercury deposition over North America (Shia et al., 1999; Seigneur et al., 2001a, 2003a, 2003c; Vijayaraghavan et al., 2003).

The modified CAMx was used by the Wisconsin Department of Natural Resources to estimate mercury deposition in the state of Wisconsin and the Great Lakes Region (Yarwood et al., 2003).

A peer review of the Wisconsin CAMx modification and application project was conducted. The model formulation was viewed as sound and the mercury mechanism perhaps the most comprehensive yet incorporated into a regional chemical transport model. There were issues identified with the prediction of wet deposition. The over prediction of total mercury wet deposition has been attributed to several factors, the most important of which is the approach implemented to derive CAMx precipitation rates from MM5 output fields (Tesche et al., 2004).

HYSPLIT

The HYSPLIT (HYbrid Single-Particle Lagrangian Integrated Trajectory) model is a complete system for computing simple air parcel trajectories to performing complex dispersion and deposition simulations. As a result of a joint effort between NOAA and Australia's Bureau of Meteorology, the model has recently been upgraded. New features include improved advection algorithms, updated stability and dispersion equations, a new graphical user interface, and the option to include modules for chemical transformations. Without the additional dispersion modules, HYSPLIT computes the advection of a single pollutant particle, or simply its trajectory.

The dispersion of a pollutant is calculated by assuming either puff or particle dispersion. In the puff model, puffs expand until they exceed the size of the meteorological grid cell (either horizontally or vertically) and then split into several new puffs, each with it's share of the pollutant mass. In the particle model, a fixed number of initial particles are advected about the model domain by the mean wind field and a turbulent component. The model's default configuration assumes a puff distribution in the horizontal and particle dispersion in the vertical direction. In this way, the greater accuracy of the vertical dispersion parameterization of the particle model is combined with the advantage of having an ever expanding number of particles represent the pollutant distribution.

HYSPLIT_4 was modified by the University of Michigan Air Quality Laboratory (UMAQL) to include basic mercury physical properties and chemical processes for use in the South Florida Mercury Science Program (Atkeson et al., 2002). Following completion of the modeling effort, it was evident that a more complete and

comprehensive mercury model was needed and UMAQL entered into a cooperative research agreement with the state of Florida and U.S. EPA to develop the CMAQ model.

A specially modified version of HYSPLIT_4 was developed and used to estimate atmospheric mercury deposition to the Great Lakes (Cohen et al., 2004; Cohen et al., 2007). Comparisons between modeled and measured wet deposition showed that HYSPLIT_4 tended to underestimate measured wet deposition measurements.

GEOS-Chem

GEOS-Chem is a global 3-D model of atmospheric composition that used meteorological information from the Goddard Earth Observing system (GEOS) of the NASA Global Modeling and Assimilation Office. It is used by researchers throughout the world on a wide variety of atmospheric composition problems, including ones associated with mercury. Research groups are using GEOS-Chem to simulate the atmospheric fate and transport of mercury on a global scale and in studying multi-pllutant air quality problems where GEOS-Chem provides the global-scale linkage to U.S. EPA's CMAQ modeling system and GEOS-Chem was used to specify the boundary conditions for the CAMQ modeling performed in conjunction with the Clean Air Mercury Rule. Management and support of GEOS-Chem is provided by the Atmospheric Chemistry Modeling Group at Harvard University.

AERMOD

AERMOD is a steady-state dispersion model intended for short range (up to 50 kilometers) dispersion of air pollutants. AERMOD was developed to improve upon and, ultimately, replace the ISC3 models as the U.S. EPA's preferred model for regulatory applications. On November 9, 2005, AERMOD was adopted by the U.S. EPA and promulgated as the preferred regulatory model effective December 9, 2005. The model includes dry and wet deposition algorithms and the PRIME downwash algorithms for addressing building wake effects. AERMOD can be applied in flat or complex terrain.

Due to its feature set, AERMOD can be used to model mercury deposition on a local scale (a few hundred meters up to many tens of kilometers). While specific guidance for configuring AERMOD to predict mercury deposition is not available, guidelines developed for mercury modeling with ISCST3 are presented in the September 2005 revision of the *Human Health Risk Assessment Protocol for Hazardous Waste Combustion Facilities* and can be adapted to AERMOD.

The dry and wet deposition algorithms included in AERMOD were developed at Argonne National Laboratory and are viewed as improvements over those used in ISCST3. AERMOD does not include the complex mercury chemistry implemented in regional models like CAMQ, CAMx, and the modified HYSPLIT_4 (HYSPLIT_4 is a trajectory model). Thus, it may be better suited for modeling mercury species with short atmospheric residence times like RGM. However, AEARMOD can be used to model the

deposition of any species of mercury as long as the assumption that no chemical reactions occur is reasonable.

5.2.2   Sampling and Analysis of Mercury Species in Precipitation and Air

Due to the complex interactions of mercury species in the atmosphere, and the relatively low levels involved, sample collection and analysis of atmospheric mercury is expensive. Consequently, the number of monitoring stations that can be deployed is small. Sampling and analysis protocols are strict, and laboratories with capabilities to successfully analyze low levels of mercury are limited. Collecting enough good data to enable mercury sourcing will be a major challenge.

5.2.2.1   Sample Location

When conducting air monitoring, consideration should be given to suspected point sources for contamination. If there is a suspected or known point source, air dispersion modeling of site emissions should be conducted to determine locations of maximum wet and dry deposition. Using the results of the modeling will allow for air monitors to place in areas with the highest likelihood of detecting emissions from that site. In addition to these maximum locations, air monitors should also be selectively placed near sensitive areas (e.g., lakes). Costs associated with these air monitors are significant, therefore, number of air monitoring stations will likely be limited by funding.

Due to the high cost of the air monitoring systems, an alternative would be to couple the use of air monitors with biomonitoring (such as moss). Similar to above, air modeling would be conducted to locate the areas of maximum deposition. At these areas, both an air monitor as well as moss samples would be placed. In addition, since the use of moss is relatively inexpensive, moss placement could be wide spread and of high density around sensitive areas (lakes, stream, etc.). The results from the moss could be used to map hot spots. Once the hot spots have been identified, air monitors could be placed in these areas to provide for more exact monitoring. It is recommended that wet sample air monitors be used that activate when precipitation begins and deactivate when precipitation ends, to allow for optimal sample collection.

5.2.2.2   Sample Collection

Typical sample collection for mercury in the atmosphere requires two types of sampling – one for studying wet and the other for dry deposition. Wet deposition sampling estimates mercury scrubbed from the air in precipitation which includes dissolved mercury ions, entrained Hg(p), and dissolved gaseous mercury (RGM and Hg^0) in equilibrium with the atmosphere according to Henry's Law. Dry deposition sampling estimates mercury that falls out in particulate form (Hg(p)), RGM, and Hg^0 vapor. Both wet and dry sampling should be performed in tandem at the same monitoring station to enable calculation of total mercury loads over the sampling period. Particulate sampling

is one of the most difficult steps in measurement of atmospheric mercury because of gas to particle conversion during sampling. This is because the RGM and Hg^0 vapor generally comprise 90-95% of the total mercury and Hg(p) is typically less than 5%. Since the amount of conversion depends on the sampling and analysis methods, estimation of Hg(p) is considered operationally defined.

Fortunately, there are good guidelines available that can be recommended for the Utah mercury protocol. Munthe (Munthe, 1996) and (OSPAR, 1997) provide guidelines for the sampling and analysis of mercury in precipitation and air. (USGS, 2004, TWRI Book 9-A5) provides guidelines for collecting and processing water samples for analysis of mercury at ultra-trace level (subnanogram per liter), that are applicable to precipitation samples, as well as surface waters. Another recommended resource is (EPA Method 1669) that is applicable to sample collection of trace metals (including mercury) in ambient water at EPA water quality criteria limits. Detailed discussions of the sample collection are deferred to the protocol for the QAPP/SOP portion of this project and only summaries will be offered for the purpose of this report.

For all sampling, risk of sample contamination is high when working at such low mercury levels. Unless extraordinary measures are taken to prevent contamination, much expense could be made for worthless data. The clean hands/dirty hands protocol discussed in (USGS, 2004 TWRI Book 9-A5, NFM 4.0.1) needs to be followed religiously. This also includes wearing lint-free, particle free clothes, double gloves, using double bagged scrupulously precleaned containers, and avoiding breathing over the samples.

For precipitation sampling (Munthe, 1996) and (OSPAR, 1997) recommend samples be collected in special precipitation samplers made of borosilicate glass or Teflon. Wide-mouth jars have been used for precipitation collection, but the risk of contamination is high once the rain or snowfall has stopped and subsequent atmospheric diffusion of Hg^0 into the sample can alter the sample. The person sampling needs to be present when the precipitation collection begins and needs to seal the jars as soon as the precipitation collection ends. A better approach is a funnel/bottle combination with a capillary tube between the funnel and the bottle to limit Hg^0 diffusion from the atmosphere, and prevent dust, birds, and insects from getting to the sample during and after it is collected. The collection bottles need to be shielded from light to avoid photo-induced reduction of mercury on the walls of the sample bottle. They also need to contain preservative (generally 2.5 mls 30% HCL (Suprapur grade)), unless filtered versus dissolved mercury speciation is desired. If so, preservative is added once filtration is completed in the field. Although simpler and less expensive from an equipment standpoint, neither of these collection methods are suitable for dry climates where precipitation events are more unpredictable. The best collector is a wet- only automated system that opens when precipitation begins and closes when it ends. Such samplers have thermal control to deal with ice and snow, as well as high temperatures in the summer. A critical step is to correlate the sample collected with parallel measurements of precipitation amounts. A standard rain gauge needs to be included with the equipment. The wet-only sampling equipment currently recommended by the US National Atmospheric Deposition Program

(NADP) with requirements discussed by Vermette (Vermette et al., 1995) are recommended for the Utah protocol.

Once collected, all samples need to be refrigerated, kept in the dark and transported and stored in double zip-lock plastic bags. Stability should be checked, but most EPA guidelines for mercury suggest 28 days holding time after collection should not be exceeded before samples are analyzed.

For sampling total gaseous mercury in air, (Munthe, 1996) and (OSPAR, 1997) recommend using gold traps with gas meters or mass flow controllers for air volume measurements. The method is based on the amalgamation of elemental, organic, and inorganic mercury with gold. Total gaseous mercury is collected on the surface of gold which can be gold wire, gold gauze, or gold coated glass beads housed in quartz tubes. For sample collection two of the traps are placed in series so breakthrough of mercury can be detected if the second trap shows mercury. A known amount of air sample is drawn over the traps. The sampling time and air volumes need to be sufficient to collect enough mercury for analysis, but not so large as to cause a breakthrough of mercury to the second trap. Typically 0.1 to 0.5 ml/min of air are drawn for 12-24 hours for total gaseous mercury concentrations in the range of 1-10 ng/m^3. The exposed traps are then protected from contamination by putting plastic caps on the tube ends, and enclosing them in firmly closed glass storage bottles containing silver wool to bind gaseous mercury diffusing into the storage vessels. Again, use the clean hands/dirty hands procedures. They are then transported to the laboratory for storage and analysis in double plastic bags to await analysis. Automated collection instruments such as the Tekran 2537A (http://www.tekran.com/) are commercially available that also analyze the mercury in the same instrument. While methods to collect the total gaseous mercury are fairly well developed, methods to determine dry deposition species including Hg(p), Hg0, and RGM are still being developed. One method to estimate dry deposition is using a Tekran ambient Hg monitoring system along with a meteorological flux tower. This data can be used to model estimated Hg dry deposition. Consultation with the Nevada Department of Environmental Protection (NDEP) may be beneficial (Carr J., 2006) to identify the latest developments to collect the separate species and reduce collection costs.

5.2.2.3   Sample Analysis

Wet deposition (from precipitation) requires very low level blanks and high sensitivity analyses, that you can't get with the usual mercury cold vapor atomic absorption methods like EPA Method 245.1. Likewise, air particulates collected from atmospheric dry deposition have very small sample weights (typically <100 ug) and also require strict blank control, and high sensitivity analyses. Methods similar to EPA Method 1631e, coupled with clean hands/dirty hands protocol (USGS, 2004, TWRI Book 9-A5) and EPA Method 1669 are recommended for air deposition studies. The analytical method typically uses more sensitive atomic fluorescence for detection rather than atomic absorption, and it employs a purge & trap system for concentration and interference removal. The (collection) trap is a gold amalgamation unit, with a second gold

(analytical) trap. The digestion stage uses BrCL for oxidation instead of permanganate/persulfate salts which are subject to higher blanks. Method detection limits down to 0.2 ng/L of mercury are typical. A summary of Method 1631e is excerpted below:

> "A 100- to 2000-mL sample is collected directly into a cleaned, pretested, fluoropolymer or glass bottle using sample handling techniques designed for collection of mercury at trace levels (EPA Method 1669). For dissolved Hg, the sample is filtered through a 0.45-:m capsule filter prior to preservation. The sample is preserved by adding either pretested 12N hydrochloric acid (HCl) or brominemonochloride (BrCl) solution. If a sample will also be used for the determination of methylmercury, it should be preserved according to procedures in the method that will be used for determination of methylmercury. Prior to analysis, all Hg in a 100-mL sample aliquot is oxidized to Hg(II) with BrCl. After oxidation, the sample is sequentially reduced with $NH_2OH@HCl$ to destroy the free halogens, then reduced with stannous chloride ($SnCl_2$) to convert Hg(II) to volatile Hg(0). The Hg(0) is separated from solution either by purging with nitrogen, helium, or argon, or by vapor/liquid separation. The Hg(0) is collected onto a gold trap. The Hg is thermally desorbed from the gold trap into an inert gas stream that carries the released Hg(0) to a second gold (analytical) trap. The Hg is desorbed from the analytical trap into a gas stream that carries the Hg into the cell of a cold-vapor atomic fluorescence spectrometer (CVAFS) for detection quality is assured through calibration and testing of the oxidation, purging, and detection systems."

For dry deposition mercury samples, EPA Method 7473 is recommended. This method also uses cold vapor atomic fluorescence detection and a two stage (collection and analytical) gold trap amalgamation configuration. Instead of using a wet oxidation stage and purge, as in 1631e, this method uses an in-line oven to drive off mercury directly from a solid sample. Upon release by heating, the gaseous mercury is passed on to the gold traps. (A summary of Method 7473 is given in the Section 4.2.3 below). Gold traps from mercury collection in air samples, as discussed above, can be put in the oven of the direct mercury analyzer or they can be externally heated and the released mercury introduced to the instrument. Sensitivity on the order of pg of mercury can be detected, and the ultimate detection limit depends on how much air was passed over the sample collection trap.

5.2.2.4 *Mercury Speciation in Precipitation and Air:*

Speciation in wet deposition samples is possible with filtered versus unfiltered samples in the field before the samples are preserved with acid. Again, the utmost care in cleanliness is needed during filtration. The filtration process removes the Hg(p) and leaves the dissolved Hg ions and methylmercury in solution. The unfiltered sample is analyzed for total mercury and the concentration is compared to the filtered sample. The Hg(p) can be calculated by difference. Methylmercury in the wet deposition samples can

be determined by methods that can specifically separate the methylmercury compound from the sample before analysis. The USGS method described in Report 01-445, 2002 for this parameter (De Wild, J.F, et al., 2002) is recommended. The method summary is excerpted below:

> "Water samples are distilled to remove potential matrix interferences. The pH of the distillate is adjusted to 4.9 (to maximize ethylation potential) using acetate buffer. The distillate then is ethylated using sodium tetraethyl borate (NaBEt4) and allowed to react for 15 minutes. After reaction with NaBEt4, the distillate is purged with nitrogen gas (N2) for 20 minutes and the ethylated mercury species are collected on a sample trap containing Carbotrap. These ethylated mercury species are desorbed thermally from the sample trap, separated using a gas chromatographic (GC) column, reduced using a pyrolytic column, and detected using a cold vapor atomic fluorescence spectrometry (CVAFS) detector. This method may be used to determine CH_3Hg+ concentrations in filtered or unfiltered water samples in the range of 0.040 - 5 ng/L. The upper range may be extended to higher concentrations by distilling smaller sample volumes or ethylating less of the distillate. It should be noted that repeated attempts to analyze reagent grade water spiked with CH3Hg+ resulted in low recoveries (40–60 percent). The reasons for these low recoveries have not been resolved; however, other mercury research laboratories also obtain similar recoveries (J. Hurley, University of Wisconsin; C. Gilmour, Academy of Natural Sciences, oral commun., 2001). Therefore, reagent water is not an appropriate water source for spiked standard solutions and should not be used for quality-assurance or quality-control purposes."

Speciation of mercury in dry deposition samples can be most easily determined using a commercially available system that determines Hg^0, RGM, and Hg(p). The instruments are available from Tekran. (http://wwwTekran.com). The Tekran Model 1130 attachment to the Model 2537 Analyzer uses a specially coated annular denuder that captures RGM while allowing Hg^0 to pass through. Coupled to the analyzer, both Hg^0 and RGM can be determined simultaneously in ambient air. The Model 1135 particulate Mercury Unit can also be attached to monitor Hg(p). The cost and training requirements are high, as noted by Carr (Carr, J., 2006) and less expensive options are under development. (see previous discussion in Section 4.2 above).

5.2.3   Air Deposition Study Alternatives

Because of the high cost associated with specialized sampling instrumentation and the sheer complexity of mercury air deposition studies, the number of sampling sites will be a challenge. An expensive network of monitoring stations is needed to gather enough data to draw realistic conclusions about the mercury problem. Consequently, alternative means to get the needed data should be explored, as discussed in the following sections.

5.2.4   Spatial and Temporal Dispersions

A low cost option exists that would allow determination of relative spatial and temporal dispersions of mercury from the atmosphere around suspected sources of mercury in Utah. The analysis of bioaccumulated mercury in indigenous mosses throughout the State may be considered. If indigenous mosses are scarce, transplanted mosses can augment the sampling grid.

Bryophytes, including mosses and liverworts, are useful for monitoring air pollution because they have no root system and all nutrients must come from the air. Mosses have good bioaccumulating ability for heavy metals and mercury, accumulating these in very high concentrations. Mulgrew and Williams (2000) state that mosses are widely available, easy to handle, and easy to determine annual growth for sampling purposes.

Lichens are also useful for monitoring mercury in the atmosphere as studied by Bargagli, and Barghigiani, (1991). The authors maintain that daily and seasonal fluctuations in concentrations of Hg in the atmosphere, caused by meteorological and environmental variables, has made it very difficult to assess Hg anomalies by conventional analytical procedures. Some species of widespread foliose lichens from an abandoned cinnabar mining and smelting area (Mt. Amiata), geothermal fields (Larderello, Bagnore and Piancastagnaio, Central Italy), and active volcanic areas (Mt. Etna and Vulcano, Southern Italy) seem to be very suitable biomonitors of gaseous Hg; especially as lichen thalli have an Hg content which reflects average values measured in air samples. The authors discuss the advantages of quantitative biological monitoring by lichens with respect to conventional air sampling in large-scale monitoring.

More recent studies performed by Krishna (Krishna et al., 2004), continue to recommend the use of lichens and mosses as an atmospheric biomonitoring tool. The authors did a carefully controlled study of exposure of mosses and lichens to various mercury species under laboratory conditions and under field conditions near a thermometer factory. (They also showed lichens and mosses can also be used as sorbent materials for the decontamination of inorganic and methyl mercury from aqueous solutions).

Since 1975 Sweden has used biomonitoring of mosses to determine heavy metal contamination throughout their country, determining the levels at five year intervals (http://www.internat.naturvardsverket.se/index.php3?main=/documents/pollutants/metall/tungmet/blymosse.html). Their internet site shows the improvement in heavy metal pollution from 1975 to current. Beginning in 1985, Norway has used this same protocol to determine mercury deposition trends throughout their country (http://www.environment.no/templates/pagewide____4130.aspx). Norway noticed similar mercury levels from 1985 to 1995 followed by a reduction in 2000. Biomonitoring for mercury deposition has been done in many countries of the world including China, Canada, Germany and the United States.

Most often, indigenous moss is collected for analysis, but for a more controlled experiment, transplanted "clean" mosses may be analyzed. At the summit of Roundtop

Mountain in Quebec, a mercury concentration in a transplanted feather moss of 81.4 ± 10.9 ppb was found after 12 months compared to 45.6 ± 10.6 ppb in the transplanted moss at the control site. At the end of this study the Roundtop Mountain sample was 248.3 ± 30.0 ppb compared to 108.3 ± 30.0 ppb at the control site (Evans and Hutchinson, 1996).

A host of indigenous mosses are available in Utah. A comprehensive study of mosses in Utah was catalogued by Seville Flowers and was first published in a book in 1973 (Flowers S., 1973). The book named "Mosses: Utah and the West" has been re-released by BlackBurn Press and is a classic of the bryologic literature, available for $79.95 from (http://www.blackburnpress.com/moutandwe.html) The book discusses 256 species in 77 genera and 18 families; a large proportion of which were discovered in Utah for the first time by the author. Another excellent study lists the mosses that are found in arid regions of the Mojave and southwest Utah. They include 81 species of bryophytes. The paper can be found at (http://heritage.nv.gov/mosses/mojavems.htm).

If the option to use mosses or lichens exercised under this protocol, the number of samples should be determined using the data quality objectives process. At least eight samples would be expected to be collected for an investigative area within a two-week period in early summer or when the new growth rate of the moss is highest to achieve the highest potential heavy-metal uptake. However, the specific number of sampling locations necessary for determining potential combustion related deposition of mercury is dependent on the estimated size of the depositional area(s). A biased sampling approach may be used if site-specific information is available, such as historic analytical mercury data for an area of concern, air-modeling results for suspected or identified combustion sources, or identified specific areas of concern (e.g., high-use recreational fishing area). If site-specific information is not available, then a random sampling approach may be employed to identify areas of concern, such as a sample grid approach (e.g., "x" number of samples per "y" distance from suspected or known source).

Moss samples should be collected, labeled, stored on ice, transported to the laboratory, and frozen until analysis. Specifics on the sampling methodology are provided in the QAPP and associated SOPs.

Analysis of mercury levels in the moss can be determined by USEPA Method 7473 using undigested plant tissue with the Milestone Direct Mercury Analyzer currently available in the Utah State laboratory. The summary of Method 7473 is excerpted as follows:

> "Controlled heating in an oxygenated decomposition furnace is used to liberate mercury from solid and aqueous samples in the instrument. The sample is dried and then thermally and chemically decomposed within the decomposition furnace. The decomposition products are carried by flowing oxygen to the catalytic section of the furnace. Here oxidation is completed and halogens and nitrogen/sulfur oxides are trapped. The remaining decomposition products are then carried to an amalgamator that selectively traps mercury. After the system is flushed with oxygen to remove any remaining gases or decomposition products, the amalgamator is rapidly heated,

releasing mercury vapor. Flowing oxygen carries the mercury vapor through absorbance cells positioned in the light path of a single wavelength atomic absorption spectrophotometer. Absorbance (peak height or peak area) is measured at 253.7 nm as a function of mercury concentration."

The sensitivity of the analyzer should be more than sufficient to analyze 0.1 g of dried moss sample. Sample homogeneity procedures may need to be developed for this small sample size.

This initial screening is expected to locate "hot spots" which can be more closely evaluated by increasing the density of indigenous moss sampling, transplanting "clean" moss throughout the hot spots for later analysis. Knowing the hot spots can aid in selective location of more expensive conventional wet and dry air deposition monitors.

Figure 5-2 . Flow Chart for Use of Moss to Locate Hot Spots.

Determine Moss Species Indigenous to Utah

↓

Determine Moss Portions to Sample

↓

Determine Frequency of Sampling and Sampling Grid

↓

Locate Mosses to be Sampled—GPS, Photographs, Questionnaire on Locale, Altitude, etc (Prior to Summer)

↓

Within Two Weeks Collect all Samples; Deliver Them to the Laboratory

↓

Freeze Samples until Analysis

↓

Analyze on Milestone DMA

↓

Plot Data on State Map and Locate "Hot Spots"

↓

For each Hot Spot, Set up Traditional Air Monitors

5.2.5   Mercury Depositional Network

The National Atmospheric Deposition Program (NADP) has set up a Mercury Deposition Network (MDN) (http://nadp.sws.uiuc.edu/mnd/) to develop an ongoing national database of total mercury in precipitation and determine the seasonal and annual flux of total mercury in wet deposition. The database is used to develop information on seasonal and spatial trends in mercury deposited to surface waters, forested watersheds, and other sensitive receptors. The MDN currently has 86 sites in operation nationally with two sites near Utah in northern and southwest Colorado, two inactive sites in northern Nevada, and one in Utah in the Salt Lake City metropolitan area. The MDN only monitors wet deposition. The NADP has recently recognized (http://nadp.sws.uiuc.edu/mdn/mtn.asp) the need to establish a new network to monitor atmospheric mercury species and mercury wet deposition events so total and dry deposition of atmospheric mercury can be monitored. This data would allow predictive-model evaluation, source-receptor assessments, and spatial-temporal trend analysis. The new proposed network will include locations that are regionally representative, areas with high levels of mercury emissions and mercury deposition, and locations within sensitive ecosystems.

5.3   Sediment

Sampling of sediments will allow for an understanding of deposition of mercury in the water body and will also allow for a better understanding of the methylation process and subsequent bioavailability of mercury.

5.3.1   Sample Locations and Numbers

Sufficient samples determined using the data quality objectives process should be collected to allow for statistical analyses of the data. It is expected that at least eight samples would need to be collected for each area of concern.

5.3.1.1   Stream/River Sediment

Streams and rivers are dynamic bodies of water. The energy of a stream is directly related to the ability of the water to transport sediment. The greater the energy, the greater the distance of sediment transport. Typically the fastest velocity of a stream is near the center of the channel. Velocity is also greater on cut bank versus point bars. Where stream velocity is slower, sediments have a tendency to fall out of suspension and accumulate. Sediment samples should be biased to these areas of higher sediment accumulation, such as along the sides of the stream on point bars and along insides of stream bends.

Samples should be collected at times of low water flow for streams or low levels for lakes. Sampling at low water levels will allow for sampling of more undisturbed sediments. For streams/rivers, sediment samples should be collected near the furthest upstream reaches and at intervals along the stream.

5.3.1.2   Lake Sediment

For lakes, sediment samples should be collected near inlets, outlets, and near the deepest portions of the lake (if allowable). If sedimentation is significant, it may be possible to collect a shallow sediment sample as well as a deeper sediment sample. Comparing the samples will allow some indication as to whether depositional history has changed with time. Samples should be collected at times of low water levels. Low lake levels indicate of low influx of water, meaning the lake has lower turbulence and turnover. These conditions support sediment falling out of suspension. Sampling at low water levels will also allow for sampling of more undisturbed sediments.

5.3.2   Methods for Determining Mercury Speciation

EPA SW-846 Method 7471 and EPA Method 245.5 are widely used laboratory methods for sediment and soil samples for mercury, with Method 7471 being the preferred method. Method 7471 allows detection of all forms of mercury including relatively insoluble, least toxic mercury sulfide HgS. However, the milder solvents used in Method 245.5 do not solubilize HgS and the Method estimates the more toxic forms of mercury. Neither of these methods are considered speciation methods, but comparison of the same samples analyzed by both methods can give an estimate on the fraction of mercury that is more toxic.

Method 7471 is approved for measuring total mercury (organic and inorganic) in soils, sediments, bottom deposits, and sludge-type materials. All samples must be subjected to an appropriate dissolution step prior to analysis. If this dissolution procedure is not sufficient to dissolve a specific matrix type or sample, then this method is not applicable for that matrix (http://www.epa.gov/epaoswer/hazwaste/test/pdfs/7471a.pdf).

Based upon the results of initial sediment analyses using Method 7471, if sediment is identified as having significant concentrations of mercury, more complete method for speciation of mercury compounds may be useful. In this case, EPA SW-846 Method 3200, which is based on selective solvent extraction or solvent phase extraction, followed by normal mercury analysis steps on the collected fractions is recommended. The summary of the method is excerpted below:

> "For the determination of extractable mercury species, a representative sample aliquot is extracted with an appropriate volume of solvent at elevated temperatures. Extraction is accomplished with the aid of either microwave irradiation or ultrasound. Following initial extraction, the resultant extracts are separated from the remaining sample matrix for analysis of extractable mercury

by an appropriate technique. The residual sample matrix may be analyzed for non-extractable mercury using an appropriate technique. The method also has provisions for the separation of the extractable mercury fraction into inorganic and organic mercury fractions or individual species. The inorganic and organic mercury fractions may be separated by using a solid-phase extraction procedure. Individual species may be separated and determined by using an HPLC or other appropriate separation device coupled to an appropriate detector. The method also has provisions for the separation of the non-extractable mercury into semi-mobile mercury fractions using sequential acid extraction and digestion."
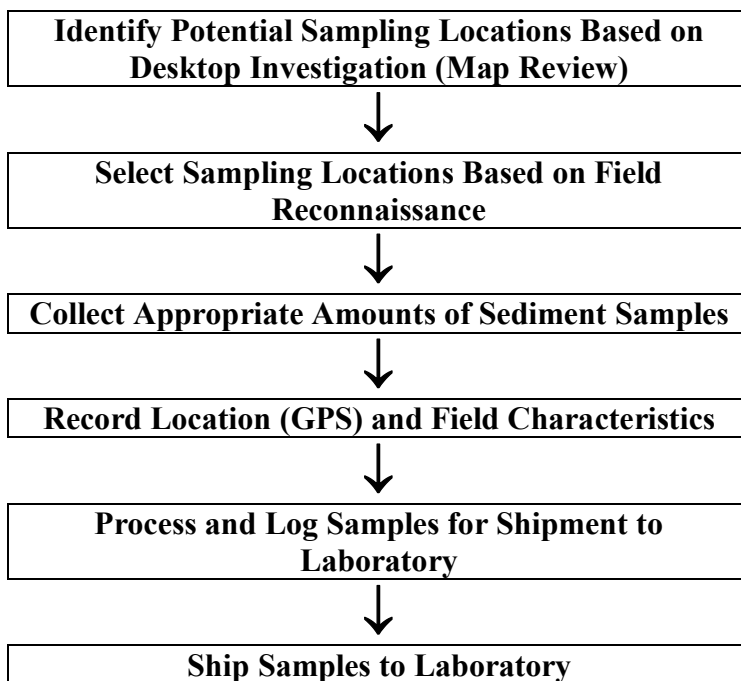
Speciation of mercury in soils and sediments by selective solvent extraction has been studied prior to Method 3200 and was shown to be a reliable, simple technique for characterizing toxic and non-toxic forms of mercury in samples. Miller, et. al, 1994, carefully studied extraction of various mercury compounds in solvents of varying strength (see http://www.epa.gov/esd/pdf-ecb/542asd95.pdf). Clean soil samples spiked with mixtures of mercury compounds were sequentially extracted with the increasingly stronger solvents and the extracts were analyzed for each fraction of mercury. Compounds could be easily separated sequentially into organic, water soluble, acid soluble, nitric acid soluble, and nitric/hydrochloric acid soluble classes. This sequence released mercury compounds of decreasing toxicity. The method was successfully applied to mercury in contaminated soils from mining in the Carson River drainage in Nevada. Most of the mercury there was found to be in the least toxic form of HgS. The method was also applied to heavily contaminated soils and sediments in the East Fork Poplar Creek site in Oak Ridge Tennessee (Gerlach, et al, 1995). That study showed a much higher proportion of mercury was in the more toxic forms that could be extracted by water and weak acid. Application of the technique to sites with low levels of mercury contamination has not been done, so the lower limits of the method are currently unknown. Another study (Slowey, et al., 2005) used sequential chemical extractions to study speciation of mercury and mode of transport from placer gold mine tailings in a legacy mining area (Clear Creek which flows into the Sacramento River and San Francisco Bay). That study saw a small fraction (3-4%) of readily soluble forms of mercury, and a much larger fraction of intermediately extractable phases that likely contain inorganic and organic sorption complexes and amalgams (75-87%) and insoluble forms such as mercury sulfide (6-20%).

Mobility of mercury from sediments and soils to surface water can be measured by EPA SW-846 Method 1312, Synthetic Precipitate Leaching Procedure (SPLP). Method 1312 is designed to determine the mobility of both organic and inorganic analytes present in liquids, soils, and wastes (http://www.epa.gov/epaoswer/hazwaste/test/pdfs/1312.pdf). Results are considered representative in a theoretical context of the mass of soluble mercury contained in surface water sediments, which may be released to surface water by dissolution.

Details on sampling methodologies and analysis are addressed in the QAPP and associated SOPs. However, the overall process is summarized in Figure 5-3 .

Figure 5-3. Flow Chart for Sediment Sampling.

Identify Potential Sampling Locations Based on Desktop Investigation (Map Review)

↓

Select Sampling Locations Based on Field Reconnaissance

↓

Collect Appropriate Amounts of Sediment Samples

↓

Record Location (GPS) and Field Characteristics

↓

Process and Log Samples for Shipment to Laboratory

↓

Ship Samples to Laboratory

5.4   Surface Water

The objective of sampling surface water is to quantify the mass of mercury contained in the suspended and dissolved loads of surface waters.

5.4.1   Sample Location and Number

Sufficient number of surface water samples should be collected to allow for a statistical analysis of the data. The data quality objectives process will be used to determine the appropriate number of samples. It is expected that at least 8 samples per area will need to be collected.

5.4.1.1   *Streams and Rivers*

In general, surface water samples should be collected away from the stream bank in the main current and should never be collected from stagnant water. The outside curve of the stream is often a good place to sample, since the main current flows toward this bank.

5.4.1.2   Lakes

A boat may be required for deep sites such as lakes. In lakes, the sample should be taken a nominal eight to ten inches below the surface of the lake and about a foot off the bottom of the lake. These measurements will provide an idea of mixing in the lake.

Samples should also be collected near inlets and outlets of the lake, to assess mercury levels coming into the lake via streams and what concentrations are being transported downstream. Since methylmercury may form better under anoxic conditions, the whole water column may need to be sampled, especially at depth. The following links will provide additional information:
http://www.springerlink.com/content/k272766371468ph3/,
http://www.springerlink.com/content/x0121n275267663h/, and
http:/also.org/lo/toc/vol_42/issue_8/1784.pdf

5.4.2   Sample Analysis

For surface water, EPA SW-846 Method 1631e for low levels and EPA Method 245.1 for moderate levels of mercury are the preferred laboratory methods.

Method 1631, Revision E is for determination of mercury (Hg) in filtered and unfiltered water by oxidation, purge and trap, desorption, and cold-vapor atomic fluorescence spectrometry (CVAFS). This Method is for determination of Hg in the range of 0.5–100 ng/L and may be extended to higher levels by selection of a smaller sample size. The ease of contaminating ambient water samples with mercury and interfering substances cannot be overemphasized. This Method includes suggestions for improvements in facilities and analytical techniques that should minimize contamination and maximize the ability of the laboratory to make reliable trace metals determinations. The detection limit and minimum level of quantitation in this Method usually are dependent on the level of interferences rather than instrumental limitations. The method detection limit (MDL) for Hg has been determined to be 0.2 ng/L when no interferences are present. The minimum level of quantitation (ML) has been established as 0.5 ng/L. An MDL as low as 0.05 ng/L can be achieved for low Hg samples by using a larger sample volume, a lower BrCl (bromine monochloride) level (0.2%), and extra caution in sample handling. The method will work well for surface waters and precipitation. A summary was provided in Section 5.2.1.3.

Both filtered and unfiltered water samples need to be analyzed to allow speciation between dissolved mercury and particulate mercury. Results of the filtered analysis will be considered representative of mercury concentrations in the dissolved phase and that is considered bioavailable in an empirical context. Unfiltered samples will be considered representative of mercury concentrations in both the suspended and dissolved loads. Amount of sample collected should be sufficient to ensure the laboratory has sufficient sample to run analyses for both a filtered and unfiltered sample.

Water quality information should also be collected at each sampling point to include the following:

- Water temperature,
- Dissolved oxygen,
- Specific conductance,
- pH,
- Salinity,
- Depth of sample, and
- Flow rate (streams and rivers).

The above parameters can be easily measured in the field, however additional parameters should be monitored in the laboratory such as sulfate, sulfide, and dissolved organic carbon. Since the mercury methylation process is driven by these additional constituents, it is important to know their concentration to fully assess the significance of mercury concentrations in water. Details on sampling methodologies and analysis are addressed in the QAPP and associated SOPs. A generalized summarization of the surface water collection process is provided in Figure 5-4.

Figure 5-4. Flow Chart for Surface Water Sampling.
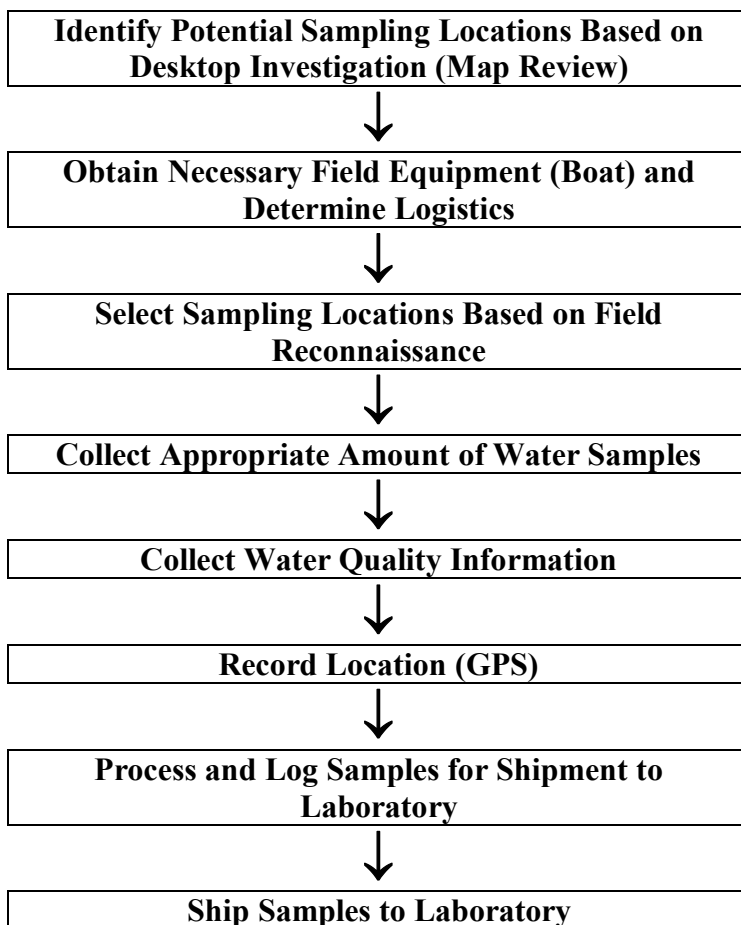
5.5   Snow Pack

Studies have shown that snow has a tremendous ability to scavenge mercury out of the air. Snow provides a good indicator of the chemistry in precipitation that occurs over the winter months. In addition, in many areas, snow pack serves as the primary recharge source for streams, lakes, and wetlands. In areas under investigation where there is snow and/or is affected by snow pack runoff, sampling of snow is recommended.

5.5.1   Sample Locations and Sample Numbers

Concentrations of mercury in snow would be expected to be variable with different concentrations detectable in the various layers of snow. In order to ascertain the amount of mercury in snow that has occurred over an entire season, snow packs should be sampled late in the season at peak snow packs and when possible, sampling should be timed to occur just prior to the spring snow melt.

According to USGS snow pack studies (USGS, 2000), sample sites should be located in clearings below tree line where snow cover is uniform. Sample locations should also be located away from plowed roads (at least 500 m) to minimize contamination from vehicles. Altitude should also be considered because the mercury to precipitation sorption rate appears to increase with altitude (Schuster, et al., 2002). Snow drifts and scoured/windblown areas should be avoided.

The number of samples to be collected is dependent on the depth of snow and the amount of visible layers of snow. Sufficient samples from each discernable snow layer should be taken to ensure a representative cross section of the entire snow pack. It is expected that near more urbanized areas, such as the great Salt Lake City valley, effects of localized inversions may be visible in snow pack.

5.5.2   Sample Collection

Because of the extremely dilute chemistry of snow at sampling sites, snow samples should be carefully collected to prevent cross contamination. USGS (2000) recommends that the bottom 10 cm of the snow pack not be sampled to avoid inclusion of forest litter and soil in the samples and that the top 5 cm of snow pack be discarded to exclude snow contaminated by activities resulting from transport to and preparation of the snowpit.

Sample analysis is similar to that for surface water samples (refer to Section 5.4.) and wet deposition precipitation samples (refer to Section 5.2.1.8). Details on sampling methodologies and analysis are addressed in the QAPP and associated SOPs. A general overview of the sampling procedure is provided in Figure 5-5.

Figure 5-5. Flow Chart for Snow Pack Sampling.

Identify Potential Sampling Locations Based on Desktop Investigation (Map Review)

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Obtain Necessary Field Equipment (Snowmobile, Snowshoes, Skis) and Determine Logistics

↓

Select Sampling Locations Based on Field Reconnaissance

↓

Collect Appropriate Amount of Snow Samples

↓

Record Location (GPS) and Field Characteristics

↓

Process and Log Samples for Shipment to Laboratory

↓

Ship Samples to Laboratory

5.5.3 Long-term Monitoring

Monitoring of annual snowpack chemistry in the study area(s) would provide a greater understanding of the effects of above-or below-average precipitation on the deposition chemistry. Continued analysis of geographic patterns of emissions sources should be a priority because of the usefulness to understanding chemical concentrations or precipitation amounts (USGS, 2000).

The constituent list could be expanded beyond mercury to include the following: major ions, ammonia, nitrate, sulfate, delta 34S, delta 18O, and delta D. These additional chemical constituents will allow for increased forensic power in differentiating mercury sources in the various watersheds of the State. However, the cost may be prohibitive. For more information, see: (Dewayne, C.L. et al. 1998) (http://www.blackwell-synergy.com/doi/abs/10.111/j.0435-3676.1998.00044.x)

5.6 Fish and Invertebrate Sampling Methodology

Fish and aquatic invertebrates are important components of both aquatic and terrestrial food chains. Invertebrates are essential to the success of an aquatic ecosystem as they represent the food base for many aquatic ecosystem species (e.g., fish, wading birds, waterfowl and wildlife). Invertebrates are good environmental indicators as they are

sensitive to chemical pollution and are fairly immobile, as compared to fish. Fish species are also an essential component of an aquatic ecosystem, as they also represent a food based for upper level species, as well as an important recreational and subsistence source for humans. Fish are good environmental quality indicators as they can be sensitive to chemical pollution as well, but their home ranges are significantly larger than that of aquatic invertebrates.

Mercury can transfer up the aquatic food chain, and bioaccumulate and biomagnify by means of direct exposure (e.g. direct contact with mercury contaminated surface water or sediment media) or through indirect exposure via ingestion of contaminated prey that has accumulated mercury. Mercury does bioaccumulate at varying rates, depending on the aquatic species and environmental conditions. As such, it is important to sample various species of both invertebrates and fish in order to understand the complete potential food chain exposure pathway. Invertebrate and fish tissue samples can provide a direct measure of accumulated mercury and can be used to infer possible exposure conditions to even higher trophic level organisms. The following sections describe the general methods to establish a sampling program involving the collection of fish and invertebrates for examining mercury tissue concentrations. These approaches were designed with the intent of collecting baseline information to initiate the investigation of the following basic questions:

- To what degree is mercury impacting invertebrates and fish communities that come into direct contact with contaminated surface water and sediment;

- What are the typical concentrations of accumulated mercury within representative species of fish and invertebrates for a select area, and;

- What are the tissue specific concentrations of accumulated mercury within representative species of fish that may become prey to higher trophic level organisms, including humans, aquatic wildlife, wading birds, and raptors among others.

The design of a sampling event or regime is dependent upon a number of variables. For the purposes of conducting biotic sampling, it is recommended that a holistic watershed approach be implemented. This approach will provide results that help to characterize the entire aquatic ecosystem and the potential resulting impact of chemical pollution. A watershed sampling approach entails the evaluation of all aquatic habitats within a watershed that are potentially impacted by mercury contamination.

As a first step, sample locations should be completed in a biased manner by focusing on areas where aquatic species occur in both background locations (e.g., sites outside the influence of anthropogenic mercury contamination) as well as in areas where mercury contamination is suspected. A simple review a topographic map or available USGS gauge station data can provide a good first indicator of where sampling locations can be established through identification of key characteristics, such as systems containing perennial water (more likely to contain fish year-round) and natural habitat

characteristics. A field reconnaissance of the potential sampling locations should be conducted to further refine areas of interest. For example, concentrations of mercury would be expected to occur in greater concentrations within fine-grain bottom substrates with larger surface areas and reducing conditions conducive to methylation of mercury (e.g. pools, ponds, among others).

There are two broad categories of freshwater aquatic environments in watershed systems: 1) flowing systems (e.g., creeks, streams, and rivers), and; 2) static systems (ponds, lakes and wetlands). Sampling approaches will vary for these two systems since the types of habitats within them are distinctly different. Summary considerations for mercury sampling within these two categories are as follows.

1. Flowing (Lotic) Systems: There are three general types of macrohabitats in flowing systems, including pools, riffles, and runs. Pools often support the most diversity of species, although there are species that may not occur in these macrohabitats. Pools are also sinks for certain contaminants, as sediment deposits accumulate in these macrohabitats. As such, pools and depositional areas should be targeted when evaluating sampling locations. Sediment-associated mercury is likely to accumulate, methylate and enter into most food chain components within pool and depositional settings, whereas riffles and runs represent environments with more constant water and sediment turnover. Therefore, the likelihood of retention of mercury contaminated sediments is lower in these macro habitats. However, riffles or runs may need to be sampled in order to obtain target fish species (Table 4-1), especially given the mobile nature of fish.

2. Static (Lentic) Systems: Macrohabitats in static systems vary based on a variety of factors, including water depth, available cover (e.g., woody debris, macrophytes, undercut banks, among others), and substrate composition. These types of environments can be more difficult to sample for aquatic organisms than flowing systems due to water depths. Techniques such as sediment core or grab samplers for collecting invertebrates, and boat electroshocking, gill nets, or line and pole methods for collecting fish. However, given that static systems are more contained than flowing systems, there is a greater likelihood that all necessary target species will be present.

The number of samples will be normally determined using the Data Quality Objectives process. At least eight samples are expected to be selected to represent both the flowing and static environment within a watershed of interest. However, the specific number of investigative sampling locations necessary for determining potential mercury contamination should be determined based on site-specific factors (e.g., size of the watershed, size of the suspected area of contamination, size of the water bodies, among many others). If possible, the sampling locations should be selected to establish a gradient of mercury contamination, which will hypothetically demonstrate the extent of contamination based on a suspected contaminant source.

Biological sampling can be accomplished by a variety of means. There are numerous documents describing various fisheries and invertebrate sampling techniques. The appropriate type of equipment for sampling is dependent upon the habitat, accessibility, and the types of species to be obtained. General references for fish sampling include Nielson, L.A. and D.L. Johnson, 1983 (Nielson, et al., 1983), and Schreck, C.B. and P.B. Moyle, 1990 (Schreck, et al., 1990), while aquatic invertebrate sampling guidance can be obtained from Rosenberg, D.M. and V.H. Resh, 1993 (Rosenberg, et al., 1993), as well as the USEPA's Rapid Bioassessment Protocols (RBP) (Barbour, et al., 1999). Samples should be collected within a specific time frame, and this may be a factor in selecting the sampling method. For example, the use of gill nets requires 24-hour sets, which can limit the ability to use a single net repeatedly within a watershed.

For fish sampling efforts, this protocol follows other guidance documents already available which focus on sampling target fish species. The collection of consistent target species allows comparison of tissue results between sites and over a wide geographic area. This approach is employed as differences in habitats, food preferences, and rate of contaminant uptake among various fish and invertebrates make comparison of contaminant monitoring results difficult unless the data are obtained from the same species. For the purposes of this protocol, the fish target species fall within two groups; game fish and bottom dwellers. This approach is problematic for benthic macroinvertebrates, and sampling for invertebrates focuses on collecting samples from distinct invertebrate habitat types to represent the target organisms. The following sections will assist in identification of the appropriate species or communities to target for sampling efforts.

Fish and invertebrate sampling locations should be co-located with any surface water and sediment sampling program. This is important in the overall understanding of fate and transport processes for mercury in the system being investigated. To a degree, temporally and spatially co-locating biotic and abiotic samples assists in examining contaminants detected between sites with differing environmental contaminant conditions by removing a level of uncertainty.

Selection of the most appropriate sampling period is very important. Preliminary recommendations are to complete sampling from late summer to early fall (i.e., August to October). The lipid content of many species, which represents an important reservoir for bioaccumulative chemicals, (Croteau, M., 2005) is generally highest during this period, and the amount of surface water dilution from high spring melt flows is lowest, and spawning periods have ceased. The lower water levels are also more conducive for sampling activities. It is important to research species spawning information because conditions vary by region and species.

Permitting associated with the collection of biological samples in the State of Utah must also be taken into consideration. Sampling fish species requires a permit from (Utah Division of Wildlife (www.wildlife.utah.gov/rules/), and the United States Fish and Wildlife Service (USFWS) if there is a potential for threatened or endangered species (T&E species) to occur in the sampling areas. The permitting process can take several

months, and an application should be submitted as soon as a sampling approach is designed and finalized. Permits for sampling in protected habitat areas (i.e., habitats required by T&E species) require USFWS review and approval. The first step is to identify if the proposed sampling areas occur in any habitat areas inhabited by T&E species. A complete listing of the current status of all threatened and endangered species as well as permitting procedures is available on the USFWS website (http://endangered.fws.gov/wildlife.html). Incidental takings of T&E species are allowed under appropriate permit conditions.

5.6.1 Approach to Fish Sampling

Fish are good indicators of long-term effects and broad habitat conditions because they are relatively long-lived and mobile. Fish assemblages generally include a range of species that represent a variety of trophic levels (e.g., omnivores, herbivores, insectivores) and habitats. Therefore, fish tend to be reflective of overall environmental health through responses displayed in community structure and composition. Fish are also at the top of the aquatic food web and are consumed by humans, making them important for in attempts to assess contamination.

5.6.2 How to Select Target Fish Species

The trophic level, length, weight and age of a fish can all affect mercury tissue concentrations. The collection of multiple species from distinct trophic levels is advantageous for describing the bioaccumulation of mercury because a more complete range of conditions and receptor organisms can be considered. The two trophic or guild groups to target for fish tissue collection include game species and bottom dwellers.

Tissue analysis of game species will provide specific data to address current mercury levels by comparison to current USEPA criteria and provide appropriate information for the link from fish tissue mercury levels and potential human health risks. Game fish are also predator species and can therefore reflect mercury bioaccumulation through the food chain (Peterson S., et al., 2007). Young of the Year (YOY) game fish, such as trout, are good indicators of short-term changes in the food chain. Their home range remains limited during their rearing period, and their primary food source is bottom dwelling macroinvertebrates. Mercury levels found in YOY samples will represent recent exposure conditions, whereas, mature fish will show mercury levels accumulated over a longer time period, including older exposures.

Benthic fish are not expected to be the most commonly harvested species for consumption in Utah. However, they can be very important from a cultural and tribal perspective. Bottom dwellers such as suckers and carp are considered desirable by southwest cultures, and these species primarily feed off vegetation growth on substrates. These species have shown an ability to accumulate high mercury tissue concentrations.

USEPA (USEPA, 2000) recommends a select list of species (Table 5-1) to represent game and bottom dwelling fish. These recommended species were developed in order to obtain a consistent tissue data base from which to compare results across large geographic regions. The game fish species selected should be based upon the area fishing/subsistence conditions. Valued fish species that provide a significant portion of the recreational or subsistent fishing population should be targeted. These species can be identified from creel census data, or license statistics, if available. Regional fisheries managers with the Utah Division of Wildlife should be contacted to identify the appropriate species for a given area.

Table 5-1. USEPA Recommended Target Game Fish and Bottom Dwelling Fish Species for Identifying Tissue Contamination. (USEPA, 2000)

Category and Family Name	Common Name	Scientific Name
Game Fish		
Percichthyidae	White bass	*Morone chrysops*
Centrarchidae	Largemouth bass	*Micropterus salmoides*
	Smallmouth bass	*Micropterus dolomieui*
	Black crappie	*Pomoxis nigromaculatus*
	White crappie	*Pomoxis annularis*
Percidae	Walleye	*Stizostedion vitreum*
	Yellow perch	*Perca flavescense*
Esocidae	Northern pike	*Esox lucius*
Salmonidae	Lake trout	*Salvelinus namacus*
	Brown trout	*Salmo trutta*
	Rainbow trout	*Oncorhynchus mykiss*
Bottom Dwellers		
Cyprinidae	Common carp	*Cyprinus carpio*
Catostomidae	White sucker	*Catostomus commersoni*
Ictaluridae	Channel catfish	*Ictalurus punctatus*
	Flathead catfish	*Pylodictis olivaris*

Cycling of mercury in the environment is facilitated by the unstable character of its metallic form and by the bacterial transformation of metallic and inorganic forms to stable methyl forms. Studies have shown that mercury concentrations in fish tissue generally increase with age, and therefore with size (length or weight) (Sveinsdottir, A.Y., and R.P. Mason, 2005). Other researchers (Peterson, S., et al., 2007) showed, in general, Hg in piscivorous genera (Northern Pike, Northern Pikeminnow, Walleye, and Smallmouth Bass for example), was more strongly related to fish length than it was in nonpiscivorous genera. The larger fish also represent the most likely organisms to be caught, kept and eaten by recreational fishers. It is therefore important to target the larger sizes of the fish captured in order to understand the potential human health implications associated with the measured mercury levels.

The Utah Division of Water Quality Standard Operating Procedure For The Collection and Preparation of Fish Tissue Samples for Mercury Analysis (Utah DWQ 7-3-06) should be followed in collection and preparing fish for mercury analysis.

Hatchery fish may have different levels of mercury than native fish of the same species and size. Their diet is certainly different and if the hatchery is carefully controlling the water quality they are raising their fish in, the exposure to mercury will be reduced. As such, even recently stocked hatchery fish may not be representative of the natural environment. The assumption that hatchery fish have low levels of mercury should be verified empirically.

5.6.3   How to Select Sample Locations

Sites selected for fish sampling should be identified using a phased process. Researchers should first gain desk top information in the form of maps, available fisheries data, flow regimes, and any other useful information to characterize a setting. Comparable flowing environments can be identified with the use of a topographic map which depicts sinuosity, gradient, altitude and flow regime (e.g., ephemeral versus perennial). Potential suitable areas for sampling can be highlighted and then targeted for review during a site reconnaissance. During the site reconnaissance a habitat characterization can be used to conduct a comparative evaluation and identification of comparable settings.

Habitat settings sampled should be comparable. Pool habitats within flowing environments are the most likely to contain mercury contamination and cycling and are the recommended areas to focus sampling efforts. The conditions of the habitat need should be recorded and generally characterized (e.g., measurement of length and width of the pool area, depths, flow/velocity, among others). In addition, the characteristics of bottom substrate, bank condition, riparian and cover should also be recorded. The USEPA RBP (Barbour, et., al., 1999) contains a habitat characterization chapter with a scoring component to aid in this process. This is a useful tool to obtain observational information when conducting site reviews for sample site locations. Each potential sampling area can be scored and compared to each other, and the proposed sampling locations with the most comparable score should be retained for the actual fish sampling.

Static environments pose unique issues when trying to find comparable settings since these habitats can vary greatly and are usually limited in number (especially in the arid west). It may be that researchers will need to default to sampling from comparable habitats within the static environments. For instance, fish sampling could be focused upon shoreline habitats as a routine, rather than venturing to open water for one sampling area, and back-water areas for others. The key is to obtain comparable target species, and identification of comparable habitats is a step towards that goal. In addition, as the size of a water body increases, the number of samples that need to be collected to characterize the setting as a whole will also increase.
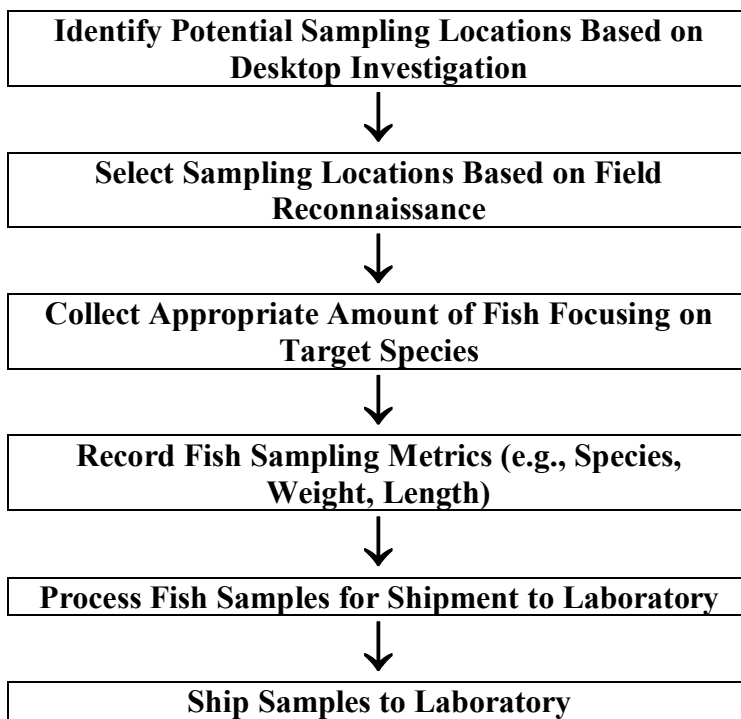
5.6.4   How to Determine the Number of Samples

As previously mentioned, the data quality objectives process will determine the number of samples, but at least eight sampling locations are expected to be required to represent both the flowing and static environment within a watershed of interest, and should include specimens from both classes of target species. The specific number of investigative sampling locations necessary for determining potential mercury contamination should be determined based on site-specific factors. If possible, the sampling locations should be selected to establish a gradient of mercury contamination, which will hypothetically demonstrate the extent of contamination based on a suspected contaminant source.

It is important to determine the potential total number of samples to be obtained so that the samplers can plan for a certain amount of additional QA/QC samples. A duplicate/replicate should be captured at a 1 to 10 frequency. An additional volume of sample should also be captured at this frequency in order to accommodate for matrix spike/matrix spike duplicate (MS/MSD) samples. Blanks will be addressed by the laboratory with the use of standard tissues, but coordination with the lab is necessary to assure that these types of samples are completed.

The overall process for sampling fish is provided in Figure 5-6.

Figure 5-6   Flow Chart for Fish Sampling.

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│   Identify Potential Sampling Locations Based on │
│              Desktop Investigation               │
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┌─────────────────────────────────────────────────┐
│     Select Sampling Locations Based on Field     │
│                 Reconnaissance                   │
└─────────────────────────────────────────────────┘
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                         ▼
┌─────────────────────────────────────────────────┐
│    Collect Appropriate Amount of Fish Focusing on│
│                 Target Species                   │
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                         ▼
┌─────────────────────────────────────────────────┐
│     Record Fish Sampling Metrics (e.g., Species, │
│                 Weight, Length)                  │
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                         │
                         ▼
┌─────────────────────────────────────────────────┐
│    Process Fish Samples for Shipment to Laboratory│
└─────────────────────────────────────────────────┘
                         │
                         ▼
┌─────────────────────────────────────────────────┐
│            Ship Samples to Laboratory            │
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5.6.5   Laboratory Sample Preparation and Analysis

The Colorado Department of Public Health and Environment Water Quality Control Division Monitoring Unit, (Colorado, 2005) provides a useful standard operating procedure for preparing fish samples for laboratory analysis. (see http://www.cdphe.state.co.us/wq/monitoring/FishTissueSOPs.pdf). Some aspects of the SOP were useful and will be incorporated into the fish preparation SOP provided from Utah's SOP. The SOP is referenced in the QAPP.

Directions are given for compositing fish portions for a given waterbody to provide representative laboratory sized portions for analysis. Once a fillet or composited fish sample is prepared for the laboratory sample portion, further preparation needs to be done before the sample can actually be analyzed for mercury. A representative 1-10 g portion can be freeze dried, then blended and analyzed as a dry tissue sample, or a 1 g portion of the wet tissue can be digested and analyzed as described in EPA Method 245.6. Wet tissue analyses for mercury can be performed down to 0.02 ug/g with this technique. Although more labor intensive, freeze drying will allow concentration of the mercury and lower detection limits on the order of 0.003 ug/g are possible. To get lower levels of mercury than that will require analysis of freeze-dried portions of fish tissue using EPA Method 7473 for analysis (see Section 4.2.3). One can then expect detection limits down to 0.05 ng/g if careful attention is paid to cleanliness and blank control. A cost-effective approach may be to screen wet tissue samples using Method 245.6 and any samples below the detection limit of the less sensitive method could then be reanalyzed using more sensitive Method 7473 on freeze-dried portions of the samples.

Speciation of mercury in fish tissue would be limited to determination of total mercury versus methylmercury. Total mercury would be determined as described in the previous paragraph, and methylmercury in tissue could be determined down to 2 ng/g, as described by Battelle Marine Sciences Laboratory (Battelle, 2006) (see http://www.battelle.org/environment/pdfs/trace-mercury.pdf).

5.7   Approach to Invertebrate Sampling

Aquatic macroinvertebrate assemblages are good indicators of localized conditions. Because many benthic macroinvertebrates have limited migration patterns or a sessile mode of life, they are particularly well-suited for assessing site-specific impacts (upstream-downstream studies). These organisms integrate the effects of short-term environmental variations since most species have a complex life cycle of approximately one year or more. Sensitive life stages will respond quickly to stress; the overall community will respond more slowly.

The specific field strategy involves the following steps, which are based on USEPA's RBP (Barbour, et al., 1999).

1. A 100 m reach that is representative of the characteristics of the stream should be selected. Whenever possible, the area should be at least 100 m upstream from any road or bridge crossing to minimize its effect on stream velocity, depth and overall habitat quality. There should be no major tributaries discharging to the stream in the study area.

2. Sampling begins at the downstream end of the reach and proceeds upstream. A total of 20 jabs or kicks should be taken over the length of the reach; a single *jab* consists of forcefully thrusting the net into a productive habitat for a linear distance of 0.5 m. A *kick* is a stationary sampling accomplished by positioning the net and disturbing the substrate for a distance of 0.5 m upstream of the net.

3. Different types of habitat should be sampled in approximate proportion to their representation of surface area of the total macroinvertebrate habitat in the reach. For example, if snags comprise 50% of the habitat in a reach and riffles comprise 20%, then 10 jabs should be taken in snag material and 4 jabs should be taken in riffle areas. The remainder of the jabs (6) should be taken in any remaining habitat type. Habitat types contributing less than 5% of the stable habitat in the stream reach should not be sampled. In this case, allocate the remaining jabs proportionately among the predominant remaining substrates. The number of jabs taken in each habitat type should be recorded on the field data sheet.

4. The jabs or kicks collected from the distinct habitats will be composited for later tissue analysis. Every 3 jabs, more often if necessary, wash the collected material by running clean stream water through the net two to three times. Remove large debris after rinsing and inspecting it for organisms; place any organisms found into the sample container. Be thorough to remove all debris. One composite sample per habitat type should be collected.

5. Transfer the sample from the net to sample container(s) (e.g., wide mouth glass jars). Measure the wet weight to be sure that at least 200 g of sample have been obtained for shipment to the laboratory for analysis. The remainder of sample(s) should be stored for later enumeration and identification.

It should be noted that the RBP approach might not be applicable to static systems if non-wadeable areas are selected for sampling (e.g., deep water areas in lakes and ponds). In the event that this occurs, alternative sampling equipment should be employed to collect aquatic macroinvertebrates. Various sampling equipment is available for this approach, including collection of sediment samples with tube cores or Ekman or Ponar bottom grab samplers. Depending on site-specific conditions, collection of enough benthic invertebrates to satisfy both laboratory and identification/enumeration needs may be impractical.

5.7.1   How to Select Target Invertebrate Species

For invertebrates it is recommended that a different approach be taken as compared to the previously described fish sampling. Rather than selecting target species, target groups based on habitat type should be obtained. The focus is to determine the invertebrate mercury body burden. The target group approach will allow for comparison between sampling locations.

However, most insectivorous species (e.g. dabbling ducks, wading birds, and fish) are not highly selective. Therefore, composite samples of multiple species that occur within a habitat type be targeted are recommended. One sample per habitat type should be obtained for each aquatic area where fish sampling occurred. For instance, if there are three invertebrate habitats per fish sampling area, three invertebrate samples should be obtained. The definition of invertebrate habitat types is provided in the following section.

5.7.2   How to Select Sample Locations

Aquatic ecosystems vary greatly, from high gradient, cobble dominated systems to low gradient streams or ponds/lakes with sandy or silty sediments. Unlike the fish sampling approach, invertebrate sampling for tissue analysis should take a more holistic approach by sampling all available habitats. Therefore, a method suitable to sampling a variety of habitat types is desired. An appropriate approach is provided in the USEPA RBP (Barbour, et al., 1999) and focuses on a multi-habitat scheme designed to sample major habitats in proportional representation within a sampling reach.

Following the RBP, benthic macroinvertebrates are collected systematically from all available instream habitats by kicking the substrate or jabbing with a D-frame dip net in appropriate microhabitats, such as woody debris/snag areas, leave packets, aquatic vegetation, and undercut banks, among others. The sampling should be proportionally representative of the habitat available. For example, if the habitat in the sampling reach is 50% snags, then 50% of the sampling effort should be extended to snags. Macroinvertebrate samples are usually subsampled due to the volume of specimens collected, and are sorted the laboratory and identified to the lowest practical taxon, generally genus or species.

The major stream habitat types listed here are those that are typically colonized by macroinvertebrates and generally support a diversity of macroinvertebrate assemblages in stream ecosystems. Some combination of these habitats should be sampled in the multihabitat approach to benthic sampling, if possible.

Cobble (hard substrate) - Cobble is usually prevalent in the riffles and runs, which are a common feature throughout most mountain and piedmont streams. However, riffles are not a common feature of most coastal or other low-gradient streams. Sample shallow areas with coarse substrates (mixed gravel, cobble or larger) by holding the bottom of the dip net against the substrate and dislodging organisms by kicking the substrate upstream of the net.

Snags - Snags and other woody debris that have been submerged for a relatively long period (not recent deadfall) provide excellent colonization habitat. Sample submerged woody debris by jabbing in medium-sized snag material (sticks and branches). The snag habitat may be kicked first to help dislodge organisms, but only after placing the net downstream of the snag. Accumulated woody material in pool areas are considered snag habitat. Large logs should be avoided because they are generally difficult to sample adequately.
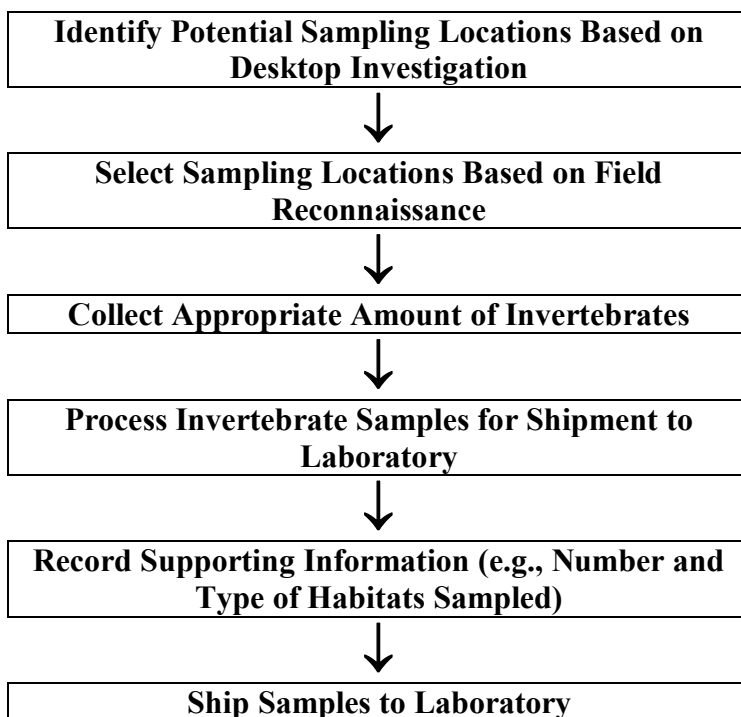
Vegetated banks - When lower banks are submerged and have roots and emergent plants associated with them, they are sampled in a fashion similar to snags. Submerged areas of undercut banks are good habitats to sample. One should sample banks with protruding roots and plants by jabbing the dip net into the habitat. Bank habitat can be kicked first to help dislodge organisms, but only after placing the net downstream.

Submerged macrophytes - Submerged macrophytes are seasonal in occurrence and may not be a common feature of many streams, particularly those that are high-gradient. Sample aquatic plants rooted on the bottom of the stream in deep water by drawing the net through the vegetation from the bottom to the surface of the water. In shallow water, sample by bumping or jabbing the net along the bottom in the rooted area, avoiding sediments where possible.

Sand (and other fine sediment) – This habitat is usually the least productive habitat for macroinvertebrate in streams, but may at times be the most prevalent. One should sample banks of unvegetated or soft soil by bumping the net along the surface of the substrate rather than dragging the net through soft substrates, as this reduces the amount of debris in the sample.

The overall process for sampling for invertebrates is provided in Figure 5-7 .

Figure 5-7 . Flow Chart for Invertebrate Sampling.

Identify Potential Sampling Locations Based on Desktop Investigation

↓

Select Sampling Locations Based on Field Reconnaissance

↓

Collect Appropriate Amount of Invertebrates

↓

Process Invertebrate Samples for Shipment to Laboratory

↓

Record Supporting Information (e.g., Number and Type of Habitats Sampled)

↓

Ship Samples to Laboratory

5.7.3   How to Determine the Number of Samples

As previously mentioned, the data quality objectives process will determine the required number of samples, but at least eight sampling locations are expected to represent both the flowing and static environment within a watershed of interest. The specific number of investigative sampling locations necessary should be determined based on site-specific factors. If possible, the sampling locations should be selected to establish a gradient of mercury contamination, which will hypothetically demonstrate the extent of contamination based on a suspected contaminant source.

Invertebrates should be collected from each invertebrate habitat type within each area identified for fish sampling. A fish sampling area may only contain one invertebrate habitat type, or it may contain many. It is up to the professional discretion of the sampler to identify representative habitat types and obtain a composite of all the benthic macroinvertebrate species within it. Each composite represents a distinct sample. It is likely that the final number of invertebrate samples collected will be three to five times more than the number of fish samples obtained. This is necessary due to the diverse types of habitats and also due to the random error introduced by composting so many different species. The increased number of samples will assist in understanding any outlying data results.

It is important to determine the potential total number of samples to be obtained so that the samplers can plan for additional QA/QC samples. Similar to the fish sampling, a duplicate/replicate should be captured at a 1:10 frequency. An additional volume of sample should also be captured at this frequency in order to accommodate for MS/MSD samples. Blanks will be addressed by the laboratory with the use of standard tissues, but this should be coordinated to assure that these types of samples are completed.

5.7.4   Laboratory Sample Preparation and Analysis

As with fish tissue, invertebrates from a waterbody can be composited, blended and reduced to give smaller laboratory sample portions, then representative 1 g portions can be selected for analysis. Since invertebrates can be freeze-dried like fish tissue, the scenario discussed above for fish in Section 4.6.5 will also work for invertebrates. Wet invertebrate tissues could be screened for mercury using EPA Method 245.6 down to 0.02 ug/g then any samples below the detection limit could be freeze-dried and analyzed by EPA Method 7473 down to 0.05 ng/g, if necessary.

Similar to speciation of mercury in fish tissue, speciation in invertebrate tissue would be limited to determination of total mercury and methylmercury. Total mercury would be determined as described in the previous paragraph, and methylmercury in invertebrate tissue could be determined down to 2 ng/g (Battelle, 2006) (see http://www.battelle.org/environment/pdfs/trace-mercury.pdf).

5.8   Soil

Soil will contain some levels of naturally occurring mercury as well as mercury as a result of atmospheric fallout or deposition. Characterization of soil is important in order to determine whether the geology/soil contains naturally high levels of mercury that as a result of erosion and surface water runoff, could contribute to mercury detected in sediments and surface water bodies. While characterization of soil is necessary, literature research indicates that soil is typically not a primary source for mercury contamination in water bodies and subsequently, fish. Sampling of soil will provide some understanding of differences in deposition of mercury between areas and will allow for an assessment of the ambient levels of mercury in soil. For comparative purposes, naturally occurring levels of mercury appear to be wide-ranging in concentration across the State of Utah, with a range of <0.01 to 4.6 parts per million (ppm).

Mercury is very mobile in the environment. In soil, mercury volatilizes and is released as a gas when in a soil body. This reaction is greatly increased when saturated soil conditions exist. Volatile forms (e.g., metallic mercury and dimethylmercury) evaporate to the atmosphere, whereas solid forms partition to particulates. These particulates are subject to mobilization through erosion of soil. Mercury exists primarily in the mercuric and mercurous forms as a number of complexes with varying water solubilities. In soil and sediments, sorption is one of the most important controlling pathways for removal of mercury from solution; sorption usually increases with increasing pH. Other removal

mechanisms include flocculation, co-precipitation with sulfides, and organic complexation. Mercury is strongly sorbed to humic materials. Inorganic mercury sorbed to soils is not readily desorbed; therefore, freshwater sediments are important repositories for inorganic mercury (Van Duren, *et. al* 2002).

The importance of ascertaining relative soil concentrations is to identify whether there are significantly higher concentrations of mercury in soil that could represent a source of contamination for downgradient water bodies. Soil sampling will also allow a determination of whether localized high concentrations of mercury are present due to geochemical properties of the geologic formations.

The sampling strategy of for soil has been developed meet the following objectives:

1. Identify possible non point sources of mercury in upland soil that may be contributing a significant mass of mercury to sediment and surface water, and
2. Estimate the total mass of mercury transported from soil to surface water and sediments.

5.8.1 Sample Numbers

Under this program, soil sampling is done to assess the general characteristics of mercury in soil. As such, a rigorous sampling approach is not warranted. However, a sufficient number of soil samples should be collected to allow for a statistical analysis of the data, consistent with the data quality objectives. At least eight samples per area are anticipated to be collected. Consideration should be given to the type of geology present. Different geologic formations may have greater natural levels of mercury than other types of rock. When collecting soil samples, care should be given to noting the formation and soil characteristics of the sample. In addition, samples should be representative of the soil and free of debris and rock.

If the number of samples is constrained by budget, composite sampling may be an option. More information on composite sampling is provided in the QAPP.

5.8.2 Sample Locations

Measurements of total mercury in soil will be considered representative of the mass of total mercury transportable to surface water by means of physical erosion (i.e., mass wasting, runoff, and wind). Locations for soil sampling should be biased locations selected to represent possible erosion pathways into surface water.

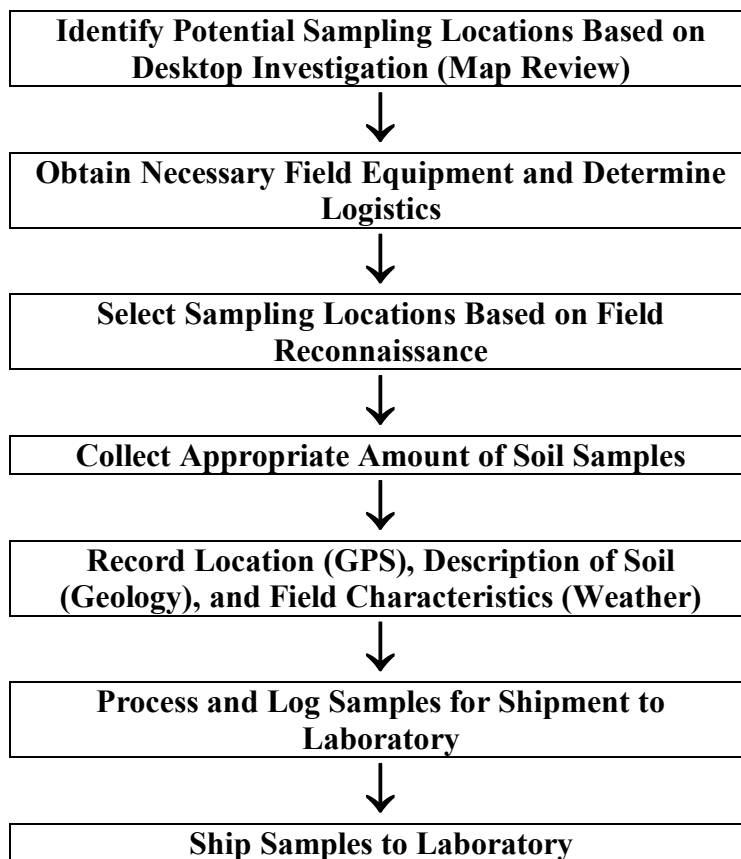5.8.3   Methods for Determining Mercury Speciation

Determining mercury species in soil is predominantly the same as the methods used for sediments (refer to Section 4.3.2). EPA SW-846 Methods 7471 and EPA Method 245.5 are the predominant laboratory methods for soil samples for mercury, with Method 7471 being the preferred method for screening.

Based upon the results of initial soil analyses using Method 7471, if soil is identified as having significant concentrations of mercury, more complete speciation of mercury compounds may be useful. In this case, Method 3200, which is based on selective solvent extraction or solvent phase extraction, followed by normal mercury analysis steps on the collected fractions is recommended. (Again, refer to Section 5.3.2).

Details on sampling methodologies and analysis are addressed in the QAPP and associated SOPs (Appendices A and B). Figure 5-8 provides an overview of the soil sampling process.

Figure 5-8. Flow Chart for Soil Sampling.

Identify Potential Sampling Locations Based on Desktop Investigation (Map Review)

↓

Obtain Necessary Field Equipment and Determine Logistics

↓

Select Sampling Locations Based on Field Reconnaissance

↓

Collect Appropriate Amount of Soil Samples

↓

Record Location (GPS), Description of Soil (Geology), and Field Characteristics (Weather)

↓

Process and Log Samples for Shipment to Laboratory

↓

Ship Samples to Laboratory

6.0   MITIGATION STRATEGIES

One of the key questions to be addressed by this protocol is, "if the sources can be identified, what can be done to reduce or eliminate these sources of mercury?" This is a difficult question to address. If the source is a non-point source, it is unclear whether any preventive measures are plausible. However, if the source is a point source, such as an identifiable industry (utility plant), air emissions controls may be an option.

On a national level, more stringent restrictions on mercury emissions are underway. On March 15, 2005, the USEPA issued the first-ever federal rule to permanently cap and reduce mercury emissions from coal-fired power plants. This rule makes the United States the first country in the world to regulate mercury emissions from coal-fired power plants. The Clean Air Mercury Rule will build on the USEPA's Clean Air Interstate Rule (CAIR) to significantly reduce emissions from coal-fired power plants --the largest remaining sources of mercury emissions in the country. When fully implemented, these rules will reduce utility emissions of mercury from 48 tons a year to 15 tons, a reduction of nearly 70 percent (http://www.epa.gov/air/mercuryrule/basic.htm).

CAIR and the Clean Air Mercury Rule are important components to improve air quality. The USEPA believes it makes sense to address mercury and other emissions simultaneously through CAIR and the Clean Air Mercury Rule. These rules will protect public health and the environment without interfering with the steady flow of affordable energy for American consumers and business. The Clean Air Mercury Rule is expected to make additional reductions in emissions that are transported regionally and deposited domestically, and it will reduce emissions that contribute to atmospheric mercury worldwide (http://www.epa.gov/air/mercuryrule/basic.htm).

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APPENDIX – QUALITY ASSURANCE PROJECT PLAN

The QAPP and associated SOPs is being provided as a separate document.